

**BENEFITS AND COST OF POTENTIAL
TIER 2 EMISSION REDUCTION TECHNOLOGIES**

FINAL REPORT

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1. INTRODUCTION

The Clean Air Act requires the U.S. Environmental Protection Agency (EPA) to consider the implementation of more stringent standards for on-highway vehicles early in the next decade. These potential standards are commonly referred to as the Tier 2 emission standards. This study, conducted by Energy and Environmental Analysis, Inc. (EEA), is intended to support the EPA in their consideration of Tier 2 standards by evaluating the potential availability of emission control technology to meet more stringent emission standards for light-duty vehicles and light-duty trucks. The issue of fuel quality, particularly fuel sulfur content, is closely associated with attainable emission levels and, therefore, specific fuel sulfur levels equal to those associated with California Phase 2 Reformulated Gasoline (CaRFG) have been assumed throughout the discussion of potential low emissions technologies in this report. To the extent that either: (1) low sulfur fuels are not available or (2) the sulfur tolerance of emission control systems is not improved, the emissions reduction potential of those systems may need to be adjusted.

Since the California Low Emissions Vehicle Program, which includes emission standards considerably more stringent than current Federal (i.e., Tier 1) standards, has been implemented and both LEVs (Low Emissions Vehicles) and ULEVs (Ultra-Low Emissions Vehicles) have already reached the market, there is a large body of published information on technologies that have been or could be used to meet these standards. Of course, the standards are partially met through the use of low sulfur CaRFG. Vehicle manufacturers are an alternative source of direct information on emission control technology and costs, but their focus on technology development has centered on meeting LEV and ULEV standards. Hence, this study unavoidably focuses on the same technologies used to meet LEV and ULEV standards in the evaluation of potential technologies to meet Tier 2 Standards. However, this study is not a LEV/ULEV standards analysis, since LEV- and ULEV-type technologies are combined into “bundles” to define achievable levels of control that differ from those of the California LEV Program. In

particular, the EPA has expressed a concern about more stringent control of NO_x emissions and, therefore, one specific technology bundle evaluated in this study is designed to provide significant additional NO_x reduction.

Section 2 of this report provides a review of published literature on technologies available to meet LEV and ULEV standards, including the California Air Resources Board's (ARB's) own biennial updates of LEV/ULEV technology progress. In addition, the section addresses differences in drivetrain parameters between light duty vehicles (LDVs) and light-duty trucks (LDTs), especially the heavier light-duty trucks that fall into the EPA's LDT3/4 category (i.e., light-duty trucks greater than 6,000 pounds gross vehicle weight).

Section 3 defines various bundles of technology that can be utilized to meet more stringent emission standards. The bundles were developed in conjunction with data provided by auto manufacturers and automotive equipment suppliers, and are utilized to evaluate potential levels of emissions control. The cost of each technology bundle was estimated using both market data and confidential inputs from auto manufacturers and equipment suppliers. However, in all instances where confidential data was utilized, it has been aggregated across manufacturers and suppliers to maintain the confidentiality of specific data inputs.

Section 4 discusses the impact of sulfur levels in gasoline on vehicle emissions performance, most notably on catalyst efficiency, and summarizes ongoing research on sulfur tolerant technology. This discussion provides the background necessary to evaluate the fuel sulfur content sensitivity of the emission reduction technologies discussed in Sections 2 and 3. The information presented on this topic was obtained from both publicly available research papers and interviews with catalyst manufacturers and researchers in the field.

2. LITERATURE REVIEW

2.1 OVERVIEW

The first element of this study was a detailed review of literature on advanced emission control technologies that go well beyond the control level offered in today's vehicles meeting Tier 1 standards. The most obvious source of literature are descriptions of technology development in response to California's Low Emissions Vehicle Program. A significant number of papers have been published by the Society of Automotive Engineers (SAE) over the last five years that deal with technology to meet either LEV or ULEV standards. In addition, the ARB publishes biennial reviews of Low Emissions Vehicle technology. Finally, EEA has been involved in two other recent investigations of advanced emission control technology for the EPA^{1,2} and has been previously provided with information on future emission control technology by major auto manufacturers in support of those investigations.

Both the ARB biennial review and the recent information received from auto manufacturers on emission control technology forecasts suggest that LEV/ULEV technology has evolved rapidly, so that research papers more than three years old provide information that is likely to be outdated and potentially superseded. While the basic technologies covered by older research papers have not necessarily changed, issues such as available alternative technologies or the means in which technologies are implemented have rendered some of the fundamental assumptions of older research papers or technology forecasts obsolete. For example, research on electrically heated catalyst (EHC) systems during the period initially following California's adoption of the Low Emissions Vehicle Program involved such concerns as pre-ignition heating and associated power demand whereas recent research demonstrates that post-ignition heating is sufficient to meet ULEV standards. Accordingly, alternator power supply has become a viable option to battery storage for EHC systems. Moreover, continuing advancements in the thermal

durability, thermal inertia, and overall activity characteristics of conventional (i.e., passive) catalysts have rendered the need for active systems such as EHCs obsolete for many applications. Due to these and similar issues, EEA focused on research from the last three years, coincident with the actual certification of LEVs (and more recently ULEVs) in California.

Separately, EEA has again conducted interviews with several auto manufacturers and automotive equipment suppliers to obtain the most recent information on technology potential. We also reviewed 1998 vehicle certification data to gain insight on the technology performance for vehicles that are currently certified to LEV or ULEV standards. Such information is presented in Section 3 of this report, while this section focuses on a review of published non-confidential literature available as of June of 1997. Fuel sulfur levels are assumed to be no greater than those of CaRFG* throughout the discussions of vehicle technology in Sections 2 and 3. This assumption is required since the performance of some technologies, most notably automotive catalysts, has been demonstrated to be sensitive to fuel sulfur. A detailed discussion of sulfur effects on emissions is provided in Section 4.

2.2 SAE PUBLICATIONS

Approximately 20 papers were obtained from SAE that ostensibly dealt with LEV- and ULEV-type technology. A review of these papers suggests that the basic technologies discussed can be categorized into four major groups as follows: (1) improvements in conventional passive catalyst performance, (2) advancements in combustion charge control through such mechanisms as improved fuel atomization and air/fuel (A/F) ratio control techniques, (3) advancements in active catalyst heating technologies, and (4) alternative aftertreatment controls such as HC adsorbers. The review also reveals that most papers focus on catalyst or other aftertreatment technology, with engine-out emissions taken as a given with the exception of minor modifications to engine calibration.

* 30-40 parts per million by weight (ppmW) on average, 80 ppmW maximum.

Four papers, from Mercedes, BMW, VW and Honda (SAE Technical Papers 940469, 940470, 940474 and 960342 respectively), deal primarily with heated catalyst systems. The Mercedes paper³ contrasted an electrically heated catalyst, a burner-based catalyst heating system, an inline adsorber, and an HC trap. In all cases, the main underfloor catalyst was retained and this catalyst was situated almost 58 inches from the exhaust manifold. Secondary air was installed to promote quicker oxidation of cold start HC, and exhaust burner or EHC heating was initiated only after start. Mercedes found all systems except the HC adsorber to be capable of meeting ULEV requirements. The HC trap was found to be the most expensive option while the cost of the EHC was dependent on whether a second battery was required. Without a second battery, Mercedes estimated that EHC system costs and burner system costs were comparable at roughly 138 percent of the cost of a conventional catalyst system.

BMW⁴ investigated catalyst heating by a separate burner, and also by an afterburner that utilized excess fuel fed into the engine after cold start (by operating at an air/fuel ratio as low as 8:1). The afterburner concept displayed poor idle behavior and difficulties during other operating modes, while the burner-equipped system required a complex controls and was judged to be significantly more expensive. VW and Pierburg⁵ also examined a fuel burner system, and came to conclusions similar to those of Mercedes and BMW. In all three cases, catalyst light-off was accomplished in 20 seconds or less, so that the actual burner-on time was very short and the associated fuel economy penalty minimal. Typically, the catalyst heating systems achieved an 85 to 93 percent reduction in HC and a 90+ percent reduction in CO, but only a 35 to 45 percent reduction in NO_x relative to an equivalent Tier 1 vehicle.

Honda⁶ reported on the use of an EHC coupled with an electrically driven air pump to provide secondary air as a potential ULEV technology. The EHC was installed ahead of the main underfloor catalyst, and required about 2.5 kilowatts (kW) of power. The EHC/secondary air combination achieved light-off in less than 20 seconds. No pre-heat was required before engine start-up. Honda also found that using an alternator-based power supply was superior to using a battery power supply system.

Nissan⁷ and Ricardo⁸ examined a broader array of emission control strategies than just aftertreatment systems. However, both papers also examined utilizing a secondary air system and electrically heated catalyst. Nissan's analysis showed that increasing cold start enrichment to an A/F ratio of 10.2 (from 13.4) resulted in decreasing HC emissions over the full FTP cycle, since the energy liberated by HC oxidation in the manifold resulted in quicker catalyst light-off. Nissan also found that gasoline properties, notably the T50 and T90 distillation points, had significant impact on cold start exhaust gas temperature. In contradiction to the conclusions of Honda, Nissan concluded that battery powered EHCs were better than alternator powered EHCs. The Ricardo paper showed the benefits of low thermal inertia exhaust manifolds and pipes. Ricardo observed a 20 percent decrease in HC but an even higher 30 percent decrease in NO_x. Ricardo also found that for large displacement engines, using an EHC and a low thermal inertia manifold was not enough to meet ULEV standards; that emission reductions during the stabilized and hot transient phases of the FTP were also necessary. Using an advanced transient air/fuel ratio controller, Ricardo found that a simple narrowing of the lambda control window did not necessarily improve emissions performance since current catalysts are optimized for current A/F control strategies and have enough oxygen storage capability to handle the A/F perturbations. Even in such cases, engine-out emissions could be reduced by improved A/F control during transients.

Seven papers were reviewed that focused on improvements to catalyst technology. In papers from Engelhard,^{9,10} development of alternative formulations to meet ULEV standards with a close-coupled and underfloor catalyst were discussed. Engelhard found diminishing returns from increasing precious metal loading beyond about 150 grams per cubic foot (g/ft³) for both the close-coupled and underfloor locations. Engelhard also found that HC performance is strongly affected by the geometric surface area of the substrate in the close-coupled position. ULEV emission levels were attained with a high cell density substrate, Pd-only catalyst in the close-coupled position and a tri-metal (Pd/Pt/Rh) catalyst in the underfloor position. A third paper by Engelhard¹¹ described the development of a ULEV version of the Ford Escort, using a Pd-only catalyst system. With the development of a new washcoat and a rich-biased calibration, the vehicle's emission levels were 50 percent lower than ULEV standards. Importantly, this

level was achieved with a close-coupled catalyst that had been aged for 24 hours by exposure to temperatures of 1,050°C.

Two recent papers by EMITEC¹² and Corning¹³ describe more severe conditions for testing close-coupled catalysts. The EMITEC paper details findings that exhaust gas temperature increases by about 100°C per meter as catalysts are moved closer to the engine while temperature transients increase from 1,000°C/minute at the underfloor location to 2,500°C/minute for some close-coupled locations. Vibration levels up to 1200 m/sec² can be encountered. Resonance effects can be particularly severe, causing failure if metal substrates resonate at engine vibration frequencies. The Corning paper focuses on the use of stronger ceramics that can be used as substrates for close-coupled catalysts. In particular, the Corning paper alluded to a finding that increasing substrate cell density appeared to significantly reduce HC emissions. However, increased cell density would lead to an increase in catalyst thermal mass unless cell wall thickness is simultaneously reduced. The Corning paper describes the development of 600 cells per square inch (cpsi), thinwall catalysts that allow for a volume reduction of 22 percent relative to a conventional 400 cpsi catalyst with the same surface area and thermal mass.

Comprehensive vehicle studies for meeting ULEV standards are described in recent papers from GM/Engelhard¹⁴ and Honda¹⁵, for a full size sport utility vehicle (LDT2) and a passenger car respectively. The GM/Engelhard system was developed for the popular GM 350V-8, used in many standard light trucks. Major modifications to the emission control system included the use of advanced adaptive electronic air/fuel ratio control, the incorporation of a mathematical model-based port air control system, dual-bank oxygen sensors at the pre- and post-catalyst locations, and an electronic secondary air pump system to inject air into the exhaust manifolds. The researchers found that additions of small amounts of rhodium, alone or in conjunction with added platinum, greatly enhances the performance of predominantly Pd catalyst systems. They also found that while catalyst-metal loading has very small effects on catalytic activity under FTP conditions, metal loading has a large effect on NO_x emissions under the more severe US06

cycle. Even with catalysts having relatively low loadings of 100 g/ft³, emissions substantially below ULEV standards were attained.

The Honda paper describes their prototype ULEV Accord in some detail. (However, it should be noted that the actual 1998 ULEV Accord differs somewhat from the prototype in its use of control technology.) The engine features Honda's VTEC variable valve timing technology which Honda claims allows substantial reduction in cold start fuel enrichment. Reduced enrichment alone contributes to a 45 percent reduction in cold start HC. Honda also uses a close-coupled catalyst that features higher Pd loading and increased cell density relative to the Tier 1 Accord catalyst. In addition, the catalyst features a double-layer structure with a Pd/Rh layer closest to the substrate and a Pt/Rh layer on the surface. The third major area of improvement is the air/fuel ratio control system which relies on a proportional control, universal exhaust gas oxygen (UEGO) sensor and an advanced "self-tuning regulator." Honda claims that the A/F ratio stays within a ± 0.2 A/F band of stoichiometric for 85 percent of the time on the FTP, as opposed to less than 50 percent of the time for the Tier 1 Accord controller.

Several other papers describe specific components for use in meeting ULEV standards. In a paper by Ford research staff,¹⁶ the effect of injection timing and fuel spray droplet size on emissions was examined. The staff found that droplet size played an important role in cold start HC emissions for open-valve injection systems, but only if injection occurred early during the intake stroke. Ford concluded that droplet sizes could effect emissions during cold operation if the droplets were large. Researchers at Hitachi¹⁷ found different effects when examining air assisted fuel injection. Hitachi varied fuel droplet size as a function of atomizer pressure and found significant benefits with air assisted atomization, both during cold start and warmed-up operation, especially at mid to high-loads. Mitsubishi¹⁸ reported on a novel heated secondary air injection system and found that heated secondary air (using a 1 kW air heater) was effective in

reducing HC and CO by 25 and 30 percent respectively over the FTP cycle (relative to unheated secondary air).

Several recent papers discuss developments in HC adsorber technology. All such systems essentially adsorb HC during cold start and desorb HC once the catalyst has reached light-off temperature. Typically, the adsorber is placed in an exhaust bypass loop between the close-coupled and underfloor catalysts. Exhaust is routed through the adsorber loop during cold start for a period of up to 100 seconds. Desorption is controlled by the flow of hot exhaust gas after catalyst light-off, but secondary air is also required to promote the oxidation of desorbed HC, making for a complex system. Corning¹⁹ described such a system and found that a fresh adsorber could reduce HC emissions in bag 1 of the FTP by 65 percent, while an aged adsorber demonstrated an HC reduction capability below 60 percent. In addition, Corning noted increases in HC emissions during desorption. Corning also described an inline adsorber system²⁰ with reduced system complexity (due to the elimination of the exhaust bypass loop), that utilized a fluidic method to divert exhaust gas away from the adsorber. Under this approach, a flow diverter controlled via injected air is used to route exhaust either through or around a hollow-cored zeolite adsorber. This system displayed equivalent or superior HC reductions over the FTP than the bypass system and could reduce system costs. NMHC levels of 0.03 g/mi on the FTP were demonstrated with an aged adsorber.

Johnson Matthey²¹ investigated HC traps in a laboratory study and found an HC trapping effectiveness of over 80 percent during the first 20 seconds after cold start. However, trapping efficiency rapidly declined to zero over the next 15 seconds. The study also found that traps were not efficient in trapping small HC molecules such as methane, ethane, and ethene. Methane and ethane emissions are less significant because they are non-reactive species.

Although there are a number of papers published recently on NO_x adsorbers, a preliminary review of the papers suggested that all of the studies have focused on NO_x adsorbers as an integral component for lean-burn combustion systems. Moreover, all of these systems have

shown extreme sensitivity to sulfur in gasoline. Since lean-burn engines are likely to be only a small fraction of total sales by 2004/2005, these papers were not considered in this analysis.

2.3 ARB'S ANALYSIS

The ARB publishes a biennial report²² on LEV and ULEV technology. These reports cover all aspects of emission control technology and, therefore, can be useful evaluating potential Tier 2 emission reduction techniques. Accordingly, EEA reviewed the ARB's November 1996 technology report for this analysis. Table 2-1 indicates the technologies included in the ARB report.

Rather than repeat all the findings of the ARB report, only a summary of the conclusions is presented. Broadly speaking, ARB expects many of the technologies listed in Table 2-1 to be on almost all cars and light trucks certified to LEV or ULEV standards. These technologies include dual exhaust gas oxygen (EGO) sensors, adaptive fuel controls targeting individual cylinder A/F ratios, reduced combustion chamber crevice volumes, sequential fuel injection (SFI) with air-assisted fuel atomizers, heat optimized exhaust pipes, leak-free exhaust systems, electronic exhaust gas recirculation (EGR) systems, and reduced oil consumption technologies. On the other hand, ARB projected limited use of the following technologies: UEGO sensors (to be used on some ULEVs and a small percentage of LEVs), electrically heated catalysts (to be used on some ULEVs), and electronic air injection (to be used only on those vehicles equipped with electrically heated catalysts). The ARB also provided a detailed estimate on the different catalyst configurations expected to be used, with the specific configuration varying with emissions certification level and number of engine cylinders. ARB's catalyst configuration forecast is as follows:

Table 2-1. LEV/ULEV Technologies Reviewed by the ARB

Dual Oxygen Sensors	Engine Calibration
UEGO Sensors	Leak Free Exhaust Systems
Individual Cylinder A/F Control	Increased Catalyst Loading
Adaptive Fuel Control	Electrically Heated Catalysts
Reduced Crevice Volumes	Electronic Air Injection
Electronic Throttle Control	Improved Washcoats
Sequential Fuel Injection	Electronic EGR
Air Assisted Fuel Atomizers	HC Adsorbers
Improved Induction Systems	Reduced Oil Consumption
Close-Coupled Catalysts	Heat Optimized Exhaust Pipes

	<u>Underfloor (UF) Catalyst Only</u>	<u>Close-Coupled (CC) Only</u>	<u>CC+UF</u>	<u>EHC</u>
<u>LEV standard</u>				
4-cylinder	40%	30%	30%	0%
6-cylinder	0%	0%	100%	0%
8-cylinder	0%	0%	80%	20%
<u>ULEV standard</u>				
4-cylinder	20%	20%	60%	0%
6-cylinder	0%	0%	80%	20%
8-cylinder	0%	0%	60%	40%

As noted, only the EHC based system was forecast to have secondary air. ARB also held out the possibility of HC adsorber systems being utilized in the 1999 and later time frame.

Interestingly, the ARB did not distinguish emission control technology as a function of engine design technology. Due to design limitations on cylinder cooling, valve and port placement, spark plug location, and combustion chamber air swirl and turbulence, older design, overhead valve (OHV) engines cannot reduce engine-out emissions as much as modern 4-valve per cylinder (4-valve) engines with compact combustion chambers. In addition, modern dual overhead cam (DOHC) engines with variable valve timing have greater advantages in being able to control internal EGR and in promoting lean combustion at part throttle (as evidenced by the Honda VTEC engine).

2.4 DESIGN REQUIREMENTS FOR LDTS

As requested by EPA, EEA conducted an analysis of design variable differences in the LDV, LDT1, and LDT2 drivetrains. This analysis was conducted by compiling detailed data on vehicle test weight (curb weight plus 300 pounds, rounded to the nearest 125 or 250 lbs), engine size, horsepower, torque, axle ratio, and the ratio of engine RPM to speed in top gear (N/V), as well as measured emissions on the FTP. The analysis relied on merging EPA test car lists²³ and EEA vehicle specification databases for 1996 and 1997 model year vehicles. No sales data were utilized as detailed configuration-specific sales data was not available at the time the analysis was

conducted. The merged databases had 1,164 records for LDVs, 329 records for LDT1s, and 542 records for LDT2s.

Table 2-2 shows the averages of specific analysis parameters for all the records in the database. The tabulated values are not sales weighted, but rather reflect simple arithmetic averages based the number of data entries in the EPA test car lists. In order to exclude such exotic cars as the high-powered Mercedes and BMW V-12s, LDVs with a test weight greater than 4,250 lbs were eliminated from analysis. No records were eliminated from analysis of the LDT1 and LDT2 databases. The data in Table 2-2 allows an assessment of basic LDV/LDT design differences through comparison of drivetrain-related parameters.

As expected, LDT1s are, on average, close to the loaded vehicle weight (LVW) cutoff of 3,750 lbs since very few LDT1s are now certified at LVWs below 3,250 lbs. Average horsepower and horsepower to weight ratio (HP/WT) are, however, higher for LDVs. The HP/WT ratio is comparable between LDT1s and LDT2s, but both classes show ratios about 15 percent lower than that of LDVs. Peak torque to weight ratios (T/WT) as well as the (torque x axle ratio) to weight ratios $((T \times AR)/WT)$ are comparable across all three vehicle groups. In contrast, both displacement (D) and displacement to weight ratios (D/WT) are significantly higher for the LDTs. The displacement to weight ratio is about 9 percent higher for LDT1s and 21 percent higher for LDT2s, relative to LDVs. In general, light trucks are powered by engines that are calibrated for low RPM torque. However, peak torque and peak horsepower are reduced by this calibration and, as a result, light truck engines appear to have lower specific power and specific torque than LDV engines. Part of this reduction is due to the fact that most LDV engines are of modern design and a large percentage of these engines have 4-valves per cylinder. Both overhead cam (OHC) and 4-valve technologies improve specific power and specific horsepower relative to the older design, 2-valve per cylinder OHV engines that remain prevalent in domestic light trucks. It should be noted that domestic models have very high market penetrations in the LDT2 class since most import trucks, except for sport utility vehicles, are LDT1s.

**Table 2-2. Average Values of Drivetrain Parameters for 1996
and 1997 Model Year Vehicles**

	LDV	LDT1	LDT2
Weight (WT)	3310	3660	4813
Horsepower (HP)	154.2	144.2	190.9
HP/WT	0.0466	0.0394	0.0396
Torque (T)	214.1	223.8	315.3
T/WT	0.0646	0.0611	0.0655
T x (Axle Ratio)	807.19	868.18	1166.68
(T x AR)/WT	0.244	0.237	0.242
T x (N/V)	8520.4	8566.55	10,443.0
(T x (N/V))/WT	2.574	2.341	2.170
Displacement (D)	2.39	2.79	4.29
D/WT x 10 ³	0.722	0.762	0.891
D x AR	9.013	10.827	15.862
(D x AR)/WT	2.723	2.958	3.285
D x (N/V)	94.93	106.68	140.78
Axle Ratio (AR)	3.77	3.88	3.705
N/V	40.52	38.38	33.13

Notes: 1. Weight measured in lbs, torque in N-m, and displacement in liters.
2. LDVs with test weights over 4,250 lbs not included.

Another factor to be noted is that (torque x axle ratio) and (displacement x axle ratio) do not follow the same trends as (torque x N/V) and (displacement x N/V). The N/V ratios for trucks are lower than those of LDVs, possibly because of larger tire sizes and numerically lower top gear ratios. The trucks appear to be geared lower in cruise mode to improve operational economics.

While basic trends can be observed from the averages computed, the relationships between individual vehicle drivetrain parameters and test weight (TW) provides more interesting insights. Regression analysis of HP and (torque x axle ratio) against test weight were performed for each vehicle class. The regressions showed significant differences in powertrain design variables as a function of vehicle weight. In general, the LDV regressions showed negative intercepts and high coefficients for test weight for each of these parameters, while LDT2 regressions showed positive intercepts and relatively low coefficients for test weight. Regression results for LDT1s were between those of the LDV and LDT2 classes. Table 2-3 presents the specific regression results.

These conflicting coefficients reflect the fact that in the LDV class, low horsepower to weight ratio vehicles with small engines tend to be small, light cars in the subcompact and compact classes. Larger cars tend to have disproportionately larger engines and offer better performance in terms of HP and torque. In contrast, the trends are exactly opposite in the LDT class. Trucks in the 4,000 to 4,500 lb LVW range tend to be personal use vehicles such as compact vans and compact sport utility vehicles. These vehicles offer performance comparable to, or slightly lower than, the performance of a midsize passenger car. Larger trucks tend to be pickup trucks, cargo vans, and very large sport utilities (such as the GM suburban) and these vehicles offer horsepower to weight and (torque x axle ratio) to weight levels comparable to or lower than those of subcompact cars. Values computed using the regressions shown in Table 2-3 illustrate the general trend as follows:

Table 2-3. Regressions Of Drivetrain Parameters Against Test Weight (TW)

LDVs:

$$\text{HP} = -115.7 + (0.0815 \times \text{TW}) \quad (r^2 = 0.708)$$

(5.1)* (0.002)

$$\text{Torque} \times \text{Axle Ratio} = -522.6 + (0.4022 \times \text{TW}) \quad (r^2 = 0.671)$$

(27.7) (0.008)

LDT1s:

$$\text{HP} = -14.2 + (0.0433 \times \text{TW}) \quad (r^2 = 0.277)$$

(14.2) (0.004)

$$\text{Torque} \times \text{Axle Ratio} = -110.8 + (0.2677 \times \text{TW}) \quad (r^2 = 0.309)$$

(82.5) (0.022)

LDT2s:

$$\text{HP} = 80.6 + (0.0229 \times \text{TW}) \quad (r^2 = 0.200)$$

(9.54) (0.002)

$$\text{Torque} \times \text{Axle Ratio} = 410.3 + (0.1589 \times \text{TW}) \quad (r^2 = 0.105)$$

(115.9) (0.024)

* Values in parenthesis indicate the standard error of the regression parameter.

	<u>HP</u>	<u>HP/WT</u>	<u>(T x AR)</u>	<u>(T x AR)/WT</u>
2,500 lb LDV	88.1	0.035	482.9	0.193
4,000 lb LDV	210.3	0.053	1,086.2	0.272
4,000 lb LDT2	172.6	0.043	1,045.9	0.261
6,000 lb LDT2	218.6	0.036	1,363.7	0.227

The emissions impacts of these trends are related to the following:

- Low torque to-weight ratio vehicles have a more difficult time meeting NO_x standards since they operate at higher average load factors and NO_x emissions increase non-linearly ratios with load. This is true for vehicles with low (TxAR) ratios , since a low axle ratio forces the engine to operate at lower RPM and higher torque.
- Large displacement engines have a more difficult time meeting HC standards since cold start fuel consumption and crevice volumes are proportional to displacement. During cold start, idle fuel consumption is a direct function of engine size.
- Older design engines, especially 2-valve OHV designs, offer lower emissions reduction potential than modern 4-valve engines.

Hence, the heavier end of the LDT2 class, generally with low horsepower to weight ratios and larger displacement engines of older design, show the least current potential for emissions reduction. The introduction of modern design engines in the LDT2 class may be forced in part, by more stringent emission standards.

2.5 SYNOPSIS OF FINDINGS

Clearly, considerable research and development related to the attainment of LEV- and ULEV-level emission rates has been undertaken over the last several years. Although in some cases, conflicting interpretations or opinions of specific technologies are evidenced, several key points can be observed.

- Auto manufacturers appear to be able to reduce gasoline vehicle emissions sufficiently to meet LEV and ULEV standards, negating any need for the introduction of new fueling technologies for emissions certification purposes.
- Most research has focused on HC control as LEV/ULEV NO_x standards appear to be achievable using basic enhancements to current Tier 1 technology.
- Although some research on engine calibration, A/F ratio control, and fuel delivery (e.g., air assisted atomizers) continues, the major focus of research and continued emission reductions is aftertreatment technology.
- Pre-start catalyst heating does not appear to be necessary for vehicles to meet ULEV standards. Although active heating systems may be necessary for LEV and ULEV compliance with some large displacement engines, post-ignition heating appears to provide sufficient emissions reduction.
- The cost of active catalyst heating systems (such as EHCs or exhaust burners) is still an issue, with differences of opinion on the relative merits of battery versus alternator EHC power supply options. Research in this area continues at a relatively intensive level as such active systems may be required for larger displacement engines to meet LEV and ULEV standards.
- Continued advances in the activity and durability of “conventional” passive catalyst systems have been observed. Research on optimizing catalyst geometry, maximizing effective surface area, reducing thermal inertia, further improving durability, and maximizing catalyst activity in ongoing and has demonstrated remarkable success, allowing a significant fraction of vehicles to achieve LEV and even ULEV emission levels without active heating systems. Durability advances have been sufficient to allow the rapid light-off, manifold mounting (i.e., extreme close coupling) of catalysts.
- Significant design differences are noted between LDV and LDT drivetrains, affecting the relative ability of each to attain low emission levels. The relatively lower (torque x axle ratio) to weight ratio of LDTs in 6000 + lb. GVW class will make stringent NO_x reductions more difficult than is the case for LDVs. LDTs also utilize larger displacement, older design engines further complicating the achievement of LDV-level emission rates. However, several older design engines could be phased out by 2004.

2.6 **REFERENCES**

1. Energy and Environmental Analysis, Inc., "Emission Control Technology Distribution, Final Report", prepared for the U.S. Environmental Protection Agency, February 10, 1997.
2. Energy and Environmental Analysis, Inc., "Assessment of Technology Costs to Comply with Proposed FTP Revisions", prepared for the U.S. Environmental Protection Agency, September 1995.
3. K. Kollmann, et al., "Concepts for Ultra Low Emission Vehicles", SAE Paper 940469, March 1994.
4. P. Longen, et al., "Heated Catalytic Converter Competing Technologies to Meet LEV Emission Standards", SAE Paper 940470, March 1994.
5. P. Oser, et al., "Novel Emission Technologies with Emphasis on Catalyst Cold Start Improvements Status Report on VW-Pierburg Burner/Catalyst Systems", SAE Paper 940474, March 1994.
6. Y. Shimasaki, et al., "Study on Conformity Technology with ULEV Using EHC System", SAE Paper 960342, February 1996.
7. K. Nishizawa, et al., "Technologies for Reducing Cold-Start Emissions of V6 ULEVs", SAE Paper 971022, February 1997.
8. O. Hadded, et al., "The Achievement of ULEV Emission Standards for Large High Performance Vehicles", SAE Paper 930389, March 1993.
9. Shau-Lin Chen, et al., "The Development of a Close-Coupled Plus Underfloor Catalyst for a ULEV Application", SAE Paper 960796, February 1996.
10. Z. Hu and R.M Heck, "High Temperature Ultra Stable Close-Coupled Catalysts", SAE Paper 950254, March 1995.
11. R. M. Heck, et al., "Close-Coupled Catalyst System Design and ULEV Performance after 1050°C Aging", SAE Paper 952415, October 1995.
12. T. Nagel, et. al. "Development of Increased Test Conditions for Close-Coupled Catalyst Applications", SAE Paper 962079, October 1996.
13. P.M. Then and U. Zink, "Advances of Durability of Ceramic Converter Systems", SAE Paper 962372E, October 1996.

14. R. M. Smaling, et al., "Washcoat Technology and Precious Metal Loading Study Targeting the California LEV MDV2 Standard", SAE Paper 961904, October 1996.
15. Honda Motor Co., "Honda ULEV Technology", 1994.
16. J. Yang, et al., "Effects of Port Injection Timing and Fuel Droplet Size on Total and Speciated Exhaust Hydrocarbon Emissions", SAE Paper 930711, March 1993.
17. G. Saikalidis, et al., "Study on Air Assist Fuel Injector Atomization and Effects on Exhaust Emission Reduction", SAE Paper 930323, March 1993.
18. H. Katashiba, et al., "Development of an Effective Air-Injection System with Heated Air for LEV/ULEV", SAE Paper 950411, February 1995.
19. J. L. Williams, et al., "By-Pass Hydrocarbon Adsorber System for ULEV", SAE Paper 960343, February 1996.
20. M.D. Patil, et al., "In-Line Hydrocarbon Adsorber System for ULEV", SAE Paper 960348, February 1996.
21. T. H. Ballinger et al., "Hydrocarbon Trap Technology for the Reduction of Cold-Start Hydrocarbon Emissions", SAE Paper 970741, February 1997.
22. California Air Resources Board, "Low Emission Vehicle and Zero Emission Vehicle Program Review, Staff Report", November 1996
23. U.S. Environmental Protection Agency, Test Car Lists for 1996 and 1997.

3. TECHNOLOGIES, LEVELS OF CONTROL, AND COSTS

3.1 OVERVIEW

As described in Section 2, emissions reductions to levels far below Tier 1 standards are possible with improvements in fuel injection, engine design, and catalyst aftertreatment technologies. A key point to be noted is that the reductions are generally attainable through a series of evolutionary improvements to existing Tier 1 vehicle technologies. Only a few revolutionary technologies such as electrically heated catalysts or HC adsorbers have emerged. As a result many aspects of technology behavior are quite similar to the behavior of current Tier 1 technologies, although the evolutionary technologies provide additional margins of emission control.

Discussions were held with several auto manufacturers on a confidential basis to better understand their approach to compliance with LEV and ULEV standards as well as to obtain their engineering insights on how these approaches may change if the relative levels of control of HC and NO_x were shifted. Similar discussions were held with representatives of catalyst manufacturers, with both auto manufacturers and catalyst suppliers providing cost data. Of course, the level of detail provided on costs varied considerably between manufacturers, with some manufacturers providing detailed component specific data and others providing more aggregated estimates.

The ARB's biennial staff report analysis served as a starting point in defining "bundles" of emissions control technology that can be used to reduce emissions below Tier 1 levels. Subsequent auto and catalyst manufacturer input was sought on both individual technologies and complete sets of technologies expected to be employed to meet LEV and ULEV standards. By and large, the disagreements on technology between manufacturers and the ARB are not dramatic, but some disagreements have cost implications. Section 3.2 discusses technology potential and

highlights areas of specific differences between auto and catalyst manufacturer's comments and ARB's technology analysis.

Since dozens of LEV models and one ULEV model have been certified for the 1998 model year, the actual technologies employed and the certification levels attained are detailed in Section 3.3. There are several surprising aspects of current LEV certified models with respect to technology and emission levels attained, and this insight can be used to refine the technology bundle definitions presented in Section 3.2. Section 3.4 discusses the potential tradeoffs between NO_x and HC emissions along with the possibility of using additional technologies to achieve specific levels of NO_x control greater than that of the California Low Emissions Vehicle Program. Finally, Section 3.5 provides a series of cost estimates for different technology bundles, including the cost of engineering design and product launch to derive Retail Price Equivalents (RPE). No fleetwide cost estimates are provided since there are no assumed target Tier 2 standards for analysis.

3.2 DEFINING TECHNOLOGY BUNDLES FOR TIER 2 COST ANALYSIS

Based upon the review of literature on available technologies to meet California LEV and ULEV standards as presented in Section 2, EEA developed a list of possible and potential emission control technologies and grouped these technologies into bundles for the purpose of evaluating associated emissions performance and HC/ NO_x tradeoffs. These bundles were then discussed with auto manufacturers to understand their emissions potential. Analysis is based on homogenous charge spark ignition (SI) engines only, as most manufacturers believe that such engines will remain the dominant vehicle power plant at least through 2005. Previous EEA work for EPA¹ revealed that some Japanese manufacturers believe the direct injection stratified charge (DISC) gasoline engine could have significant market share by 2005 (in the range of 10 to 20 percent), but DISC engines must be considered separately and are not part of this analysis.

Engine Technology - Advanced engine designs can reduce engine-out emissions and hence, may be capable of meeting standards using less aftertreatment or of meeting more stringent standards

than current Tier 1 engines. SI engines can be designed for low engine-out emissions using modern fast-burn combustion chambers, advanced port design to control A/F mixture swirl and turbulence, and low oil consumption designs for valve seals and piston rings. These advanced combustion chamber designs can be viewed as passive systems, but engines can also utilize active low engine-out emissions systems such as variable valve timing and lift. Virtually all engines regardless of design vintage can, and will likely be updated to have fast-burn combustion chambers and low oil consumption ring and valve seal designs. However, designs incorporating 4-valve heads offer additional advantages in controlling air flow into the combustion chamber as well as in the overall compactness of the chamber. As a result, EEA broadly classified engines into the following three categories for evaluating emissions reduction potential:

- Older 2-valve OHV or OHC designs
- Modern 4-valve OHC or DOHC designs
- Modern 4-valve designs with variable valve timing and lift

Manufacturers did not uniformly agree that OHV engines possess any inherent emissions disadvantages relative to OHC engines, but did agree that the design vintage of the engine was an important variable. While the combustion chamber design of an older engine model can be updated, manufacturers stated that engine layout restricts part placement, spark plug location, and the location of cylinder cooling jackets, making it difficult to update an engine to produce engine-out emissions as low as is possible with modern designs. In this context, it should be noted that most imported vehicles have more modern engines, due to shorter product life cycles which allow for the more rapid introduction of newer technologies and corresponding turnover of existing technologies. Even Ford and Chrysler passenger car engines have moved to modern designs in the last few years. Only GM offers a significant number of older-design passenger car engines and we expect that this could remain the case throughout the early-2000 time frame. Domestic light trucks represent a more significant market in which older-design engines continue to be dominant. Only Ford is moving ahead with modern-design OHC light truck engines, being likely to phase-out all OHV models in this class by the 2001-2002 time frame. GM and Chrysler are likely to update their older OHV designs, but still retain the basic block layout. At present, only Honda offers a variable valve timing and lift controlled engine (the VTEC engine), although

some manufacturers have introduced variable timing designs. Specific emission control technologies relating to the intake of air and fuel and the aftertreatment of exhaust, that are applicable to all homogenous charge SI engines regardless of design or age, are discussed below.

Fuel Injection (FI) - Most manufacturers do not expect any major changes in fuel delivery systems beyond sequential fuel injection (SFI) and believe that all non-sequential multi-port fuel injection (MPFI) systems will be converted to SFI systems by the early-2000 time frame. Hence, there are no specific variations to be considered for this technology.

Air/Fuel Mixture Preparation - Most current technology engines rely solely on the mechanical features of fuel injectors to promote fuel atomization, although some import models do make use of air-assisted atomization. Manufacturers generally do not believe that air-assisted atomization is helpful (from an emissions reduction standpoint), except in isolated cases. However, recent research papers have claimed reductions in cold start cranking time and HC emissions during the first 50 seconds after start. Although Honda's ULEV Accord does feature air-assisted atomizers, some manufacturers stated that the benefits are engine dependent and influenced by both port and injector placement as well as spray location. Heated spray targets (currently used in some flexible fuel vehicles) have also been found to be of limited value, and it is therefore believed that a minority of future vehicles will feature either air-assisted atomization or fuel spray heaters. Split intake manifolds (with separate air runners for each valve) are likely to become more common with the increasing use of 4-valve per cylinder engines and high air velocities in each runner will assist fuel atomization. Hence, two types of intake systems can be considered, one featuring variable volume runners and the other a more standard fixed runner system. In general, however, manufacturers believe that associated emission benefits are quite small, so that specific consideration of each of the alternative systems in a technology bundle is not necessary.

Electronic Controls/Diagnostics - Significant advances in electronic engine control are likely to continue to occur. Adaptive control is a very general name applied to a number of strategies that utilize software to sense and adjust engine operation to long term changes in engine behavior, fuel

quality, and ambient conditions. It is difficult to define exactly what this term implies and even more difficult to identify its implementation in specific vehicles. Adaptive controls of some type have been phased-in already on most vehicles over the last eight years. For this analysis, however, we define the system of interest as one being able to control air/fuel ratio to within ± 0.2 A/F of stoichiometric for over 85 percent of the FTP cycle (as per Honda's ULEV Accord), which may also require more advanced linear oxygen sensors as described below. Since such a system is largely based on software changes, the ability to control A/F to these levels is largely a function of other components such as universal exhaust gas oxygen sensors.

Exhaust Air/Fuel Ratio Sensors - Manufacturers have elected to use dual exhaust gas oxygen (EGO) sensors on all new vehicles to accomplish the catalyst monitoring requirements of EPA's (and ARB's) on-board diagnostic rules. As a result, most low emission vehicles could incorporate improved control algorithms using the combined features of these dual sensors. The second oxygen sensor, placed downstream of one or more catalysts in the exhaust system, can be used to monitor and adjust for deterioration of the front primary sensor, thereby allowing for the maintenance of more precise fuel control. Should the front sensor, which operates in a higher temperature environment, begin to exhibit slow response or drift in its calibration point, the second sensor can be relied upon to modify the fuel system controls and compensate for these front sensor aging effects. By placing the second sensor further downstream from the hot engine exhaust, where it is also less susceptible to poisoning, the rear sensor may not be likely to age significantly over the life of the vehicle, allowing good fuel control as a vehicle ages.

The universal exhaust gas oxygen (UEGO) sensor, also called the 'linear oxygen sensor', could replace conventional oxygen sensors. Vehicles that employ proportional A/F control strategies may utilize one or more UEGOs for fuel control in lieu of conventional oxygen sensors. Conventional oxygen sensors only determine if an engine's A/F is richer or leaner than stoichiometric, providing no indication of how rich or how lean the A/F ratio actually is. In contrast, UEGOs are capable of recognizing both the direction and magnitude of A/F transients as the voltage output of the UEGO is "linear" with changing A/F (i.e., each voltage value

corresponds to a certain A/F). Therefore, proportional A/F ratio control is possible with the use of UEGO sensors, facilitating faster response of the feedback control system and tighter control of A/F ratio.

Manufacturers are of mixed opinion about UEGO sensors. Some manufacturers feel that improved conventional (i.e., non-linear) EGO sensors using the new “planar” technology* offered significant improvement over UEGO sensors in terms of warm-up time and speed of response, so that much of the linear response benefit of UEGO sensors could be offset. Moreover, these advanced non-linear sensors would be much less costly than UEGO systems. Hence, it may be possible to reduce the cost of some systems that are currently using UEGO sensors.

EGR - EEA expects that the majority of vehicles will continue to utilize EGR, although a small minority may be certified without EGR. When the supplemental FTP (SFTP) regulations take effect, EGR use at high loads is expected and EGR systems will be either electronically actuated or make use of a vacuum reservoir. (Some manufacturers believed that the SFTP regulations could be met with mechanical EGR systems). The use of high swirl, high turbulence combustion chambers can allow the amount of EGR to be increased from current levels of 15 to 17 percent, resulting in the potential for decreased engine-out NO_x emissions.

Manufacturers comments to EEA did not specifically address the interaction between SFTP and LEV/ULEV requirements. However, manufacturers did not uniformly believe that electronically controlled EGR was necessary to meet LEV/ULEV standards, and at least one manufacturer believed that backpressure EGR was adequate. Manufacturers also noted that higher EGR levels result in loss of control of A/F ratio due to the wide temperature fluctuations of EGR and response delays in the system. Several manufacturers suggested that for some vehicles, a no-EGR system may be preferable since the NO_x benefit of improved A/F control may be

* Planar technology EGO sensors are advanced design sensors in which electrodes are constructed in a thin rectangular arrangement possessing significantly lower thermal inertia than conventional “thimble” sensor designs.

enough to offset the NO_x increase from reduced EGR. Indeed, the Honda Civic LEV has no EGR system.

Catalysts - Significant changes in catalyst formulation, size, and design are possible. In terms of noble metal use, the use of palladium (Pd) catalysts is likely to increase for close-coupled applications. Palladium catalysts, however, are less resistant to poisoning by oil- and fuel-based additives than conventional platinum/rhodium catalysts. The expectation is that palladium catalysts will be used in the close-coupled locations while conventional or tri-metal (palladium/platinum/rhodium) catalysts will continue to be used in underfloor applications. As palladium technology improves, a single close-coupled catalyst could replace both catalysts. New Pd-only catalysts are now capable of withstanding 1050_C exposure and, as a result, can be moved very close to the exhaust manifold.

EEA had previously forecast that catalyst volume and/or noble metal loading would need to be increased to provide a 20-30 percent increase (on average) in active catalyst surface area to meet the needs of the revised high load supplemental FTP cycle.² While conventional FTP emissions may not be significantly impacted, this increase in catalyst volume could significantly reduce emissions over non-FTP cycles, especially during high load operation. Even over the FTP cycle, however, larger catalysts could provide better control of NO_x in synergy with tighter control of A/F ratio.

While auto and catalyst manufacturers generally agree with these trends, they did raise several issues of clarification. First, there is general agreement that tri-metal (Pd/Pt/Rh) and layered catalysts could be used in both close-coupled and underfloor applications, or alternatively, that a single tri-metal catalyst in a semi close-coupled location could do the job of both catalysts. Second, manufacturers are examining new thin wall substrates to develop high cell density, low thermal mass catalysts for the close-coupled location. Cell densities of 600 cells per square inch (cpsi) have been commercialized, and research on 900 cpsi catalysts has been progressing. Third,

much of the research on close-coupled and increased cell density catalysts has focused on HC control and, therefore, is not necessarily transferable to a NO_x-biased control strategy .

Some manufacturers believed that electrically heated catalysts (EHC) could be used in a limited number of engine families, mostly large displacement V-8s where cold start emissions are difficult to control. Other experts believe that the EHC is an interim solution and could be replaced by a variable insulation catalyst, wherein a vacuum insulation device would be activated at vehicle shutdown, permitting the catalyst to retain heat for several days. Essentially the EHC would almost eliminate cold start HC emissions, while the variable insulated catalyst would be similar to EHCs for soak periods of up to 24-36 hours. However, with continuing improvements in conventional catalyst light-off time, thermal durability, and overall activity, manufacturers conceded that EHCs may become unnecessary in all cars in the next few years.

Hydrocarbon and NO_x adsorbers/traps are also a possibility but manufacturers are quite pessimistic about independent adsorber systems. There are three principal methods for incorporating the adsorber into the exhaust system. The first is to coat the adsorber on the catalyst substrate. The advantage is that there are no changes to the exhaust system required, but the desorption process cannot be easily controlled and usually occurs before the catalyst has reached light-off temperature. The second mechanism locates the adsorber in parallel with the catalyst and includes a series of valves that route the exhaust through the adsorber in the first few seconds after cold start, switching exhaust to flow through the catalyst thereafter. Under this system, mechanisms to purge the trap are also required. The third mechanism places the trap at the end of the exhaust system, in parallel to the muffler, because of the low thermal tolerance of adsorber material. Again a purging mechanism is required, but adsorber overheating is avoided.

Manufacturers have not developed any reliable methods for diagnosing inoperative adsorbers and are reluctant to proceed with HC adsorption technology. Moreover, catalyst manufacturers suggested that current close-coupled catalysts could have some adsorber capability integrated into their design. NO_x adsorbers have been researched, but are generally recognized as a control

device for lean-burn engines since NO_x desorbs from current designs during rich or stoichiometric operation. As a result, neither auto or catalyst manufacturers had much to say about the use of NO_x adsorbers for current SI engine emissions control, but this may partly be in response to ARB's focus on HC emissions.

Secondary Air Injection - Air pumps, either electronically driven or engine driven, to provide secondary air during periods when the engine is operating rich (i.e. during cold start) are already in use in some cars. In fact, secondary injection of air into exhaust ports after cold start, coupled with spark retard, can promote combustion of unoxidized HC and CO in the exhaust manifold and also increase the warm-up rate of the catalyst. It is also possible that secondary air will be required with the use of adsorbers or traps to provide excess air required for oxidation of HC during the desorption phase. On the other hand, there are alternative strategies to provide excess air during desorption, such as lean operation (desorption occurs after engine warm-up), so that air pumps may not be necessary for these applications. At this time, manufacturers believe that most engines will require port secondary air injection to meet ULEV HC standards, while some older design OHV engines could require air injection to meet LEV standards.

Other Technologies - There are several technologies that can provide modest benefits in emissions, but that may be required to maximize emission potential. The insulated or dual wall exhaust pipe can help in retaining heat, as can a more leak free exhaust system. However, as catalysts move closer to the engine, the benefits of insulated exhaust pipes diminish rapidly. Another possibility is drive-by-wire, where mechanical throttle operation is replaced with an electronic throttle control system, allowing for more accurate and "appropriate" throttle operation under transient vehicle operating conditions. It is not clear if drive-by-wire technology can significantly aid in reducing emissions when fuel system response has been improved to the levels found in the Honda Accord VTEC engine currently certified to the ULEV standards. Engine heat "batteries", which are passive systems capable of storing engine heat for several days following vehicle shut-off, may be an option for minimizing catalyst light-off time and cold start emissions under most vehicle starting conditions. Such heat batteries have been tested by EPA in

the past and can also provide some customer convenience benefits such as warm interior air immediately following vehicle start. However, the heat battery technology is quite expensive and the emissions benefits decline as conventional technologies continue to improve. As a result, neither drive-by-wire or heat batteries may ever be introduced on mass market vehicles, due to emission regulations. However, some limited luxury vehicle application of either technology could occur for other reasons such as comfort or driveability.

Based on those considerations, EEA has defined technology bundles with the potential to meet Tier 2 standards that are in LEV/ULEV range, but could incorporate different HC/NO_x tradeoffs. The specific bundles are presented in Table 3-1. Differences in engine size and number of cylinders will affect the number of catalysts used and costs for specific vehicle applications, but the conceptual technology bundle itself should be accurate across models.

3.3 TECHNOLOGY AND EMISSIONS OF CURRENT (1998) LEV CERTIFIED VEHICLES

There are over 20 engine families currently meeting LEV certification requirements for LDVs and LDTs and 11 medium duty engine families (of which three are CNG powered) that meet the LEV (or proposed SULEV) standards. EEA examined the technologies on the LDV and LDT models using manufacturer certification submissions. Not all of the submissions were available to us at the time of this study and, therefore, only data on 12 engine families (9 LDV models and 3 LDT models) were reviewed. The intent of the review was to identify the incremental hardware changes in LEVs relative to Tier 1 vehicles. Since manufacturer submissions are confidential, detailed model-by-model differences derived from this source cannot be publicly discussed. However, the broad general trends are presented below. When possible (i.e., when details are publicly available), model-specific data is included in the discussion.

For the majority of models examined, hardware differences are almost completely related to exhaust aftertreatment and A/F ratio control. The major difference in aftertreatment is the addition of a close-coupled catalyst in LEVs to supplement the underfloor catalyst used on Tier 1

Table 3-1. Technology Bundles For LEV/ULEV Levels of Emissions Control

Engine	Old design 2-valve	New design (4-valve and 2-valve)	New design 4-valve/VVT
Fuel System	SFI	SFI	SFI
Atomization	Air-Assist in some	Air-Assist in some	Air-Assist in some
Secondary Air	Pump	Pump or None	Pump or None
Catalyst	Closed-coupled (CC) + Underfloor (U)	CC only or CC + U	CC only or CC + U
Cold Start Catalyst	EHC or Adsorber	None or Adsorber	None or Adsorber
Oxygen Sensor	Heated EGO or UEGO	Heated EGO or UEGO	Heated EGO or UEGO
Exhaust Pipe	Insulated to CC Catalyst	Insulated to CC Catalyst	Insulated to CC Catalyst
EGR	Electrically Actuated or Backpressure	Electrically Actuated or None	Electrically Actuated or None

vehicles. In almost all cases, the underfloor catalyst volume and precious metal loading are not influenced in a significant way. Underfloor catalyst volume even increased in some models in spite of the addition of a close-coupled catalyst. Other catalyst differences are quite significant as follows:

- Total catalyst volume (close-coupled plus underfloor catalyst) is 60 to 120 percent higher than total catalyst volume for an equivalent Tier 1 model except in three specific cases.
- Most catalysts even in the close-coupled location, are still of the platinum/rhodium type with palladium catalysts used only by certain manufacturers,
- No trend could be observed in catalyst loadings for either the close-coupled or underfloor locations. Some manufacturers use lightly loaded catalysts (in the range of 100 g/ft³ or less) while others use very highly loaded catalysts (up to 250 g/ft³) comparing only among Pt/Rh catalysts.
- Except for the Accord ULEV model, catalyst cell density levels are in the 300 to 400 cpsi range.
- Catalyst volumes do not decrease in inverse proportion to loadings. Total precious metal content (in grams) is generally higher for vehicles with highly loaded catalysts, regardless of catalyst size.
- There appears to be an inverse correlation between emissions certification levels and precious metal loadings, although the sample size is too small for any statistical confirmation.

Outside of these catalyst changes, the differences are not substantial between LEV and Tier 1 certification engine families. Only 3 of the engine families listed any special exhaust manifold or exhaust pipe heat insulation (although data on several other models was not very explicit in this regard) and with the exception of the Toyota Camry (4-cylinder) LEV and Honda Accord ULEV models, all LEVs appear to use conventional oxygen sensors. The Accord and Camry models use the UEGO sensor for proportional control, and some LEV models using conventional oxygen sensors in V-6/V-8 engine powered models also use an additional sensor (one for each cylinder bank) relative to the equivalent Tier 1 model. Details on calibration strategy differences could not be obtained from the certification submissions. Only one LEV model of the 12 examined utilized electronic air injection. (Many Ford LEV models use air injection but detailed data on these vehicles was not available to us within the time frame of this study). This model is discussed below with the other exceptions to the typical hardware changes.

As noted, only the Honda Civic LEV model and the Honda Accord ULEV model do not use both a close-coupled and underfloor catalyst. The Civic uses a single underfloor catalyst with relatively high precious metal (Pt/Rh) loading. It is also unusual in that it is the only LEV model examined that does not utilize EGR. All other models use EGR of some type, ranging from simple backpressure EGR to more complex electrically actuated, computer controlled EGR. Even without EGR, the Civic's NO_x emissions are very low and are, in fact, at the low end of the observed range of NO_x emissions for LEVs.

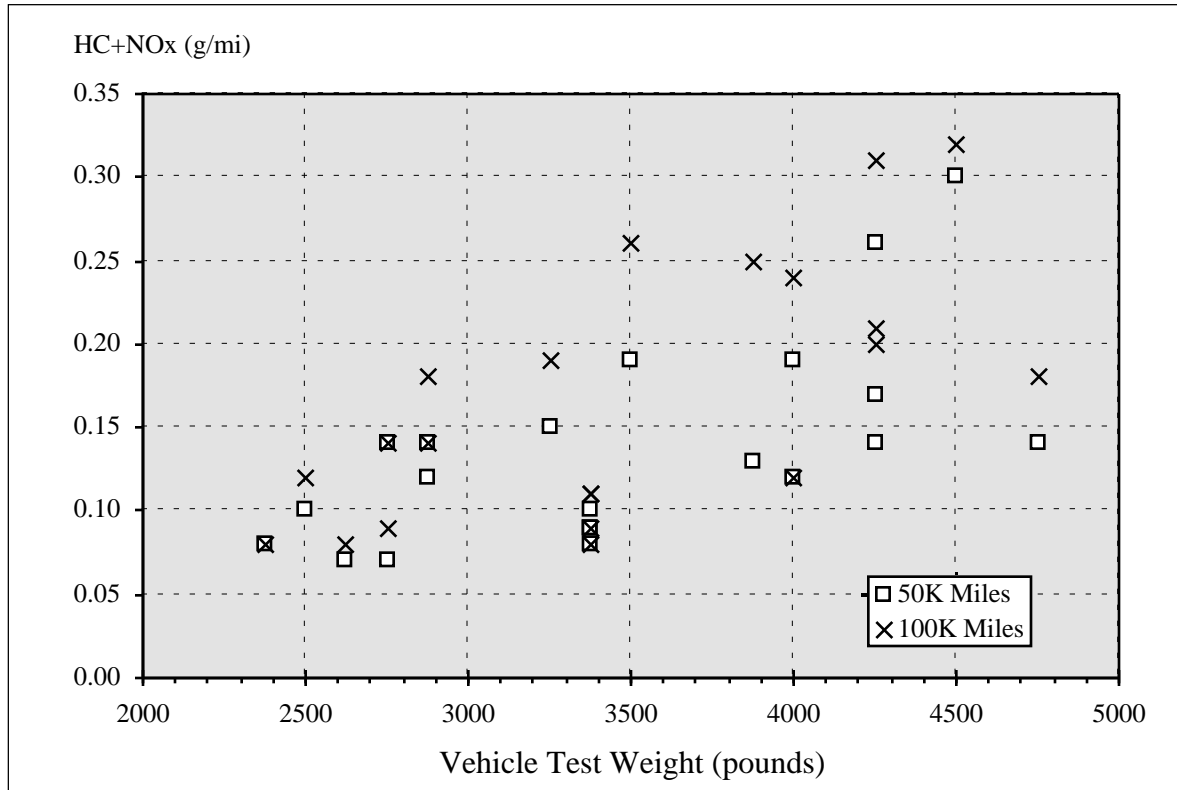
The Honda Accord ULEV is a unique design, as it's engine utilizes one of the few variable valve timing systems available today. In particular, Honda claims that VVT allows the Accord ULEV to be calibrated lean at cold start, and the engine actually operates at 16:1 air fuel ratio at cold start, instead of the more common 13:1 air-fuel ratio. The lean calibration may also be made possible by (1) air assisted atomizers for fuel injection (2) an advanced controller that features individual cylinder air-fuel ratio control and dynamic feedback adjustment during transients and (3) a fast response UEGO sensor. The Accord ULEV uses a palladium only underfloor catalyst with high cell density (600 cpsi) and a insulated dual wall exhaust pipe from the manifold to the catalyst (Note that there is no close-coupled catalyst). Honda has publicly stated that the system retail price effect is less than \$300, but this cost does not include the cost of the VVT system.

The only model with air injection among the 12 models examined is the Mercedes E320. This V-6 powered model uses dual close-coupled catalysts and an underfloor catalyst, and attains exceptionally low HC emissions for a 4000 lb test weight vehicle. Indeed, the ULEV Accord has certification emission levels of 0.03 HC and 0.06 NO_x (g/mi) at 100,000 miles while the E320 model attains HC emissions of 0.02 HC and 0.10 NO_x. These levels are consistent with some of the data in the reviewed literature (Section 2) that suggested that using an air pump with enrichment of A/F ratio and spark retard, allows very quick light-off of the close-coupled catalyst enabling certification to ULEV standards (the Mercedes E320 could qualify for ULEV certification).

The certification levels of the LEV vehicles relative to applicable standards are another area of interest. Prior to 1994, manufacturers would target certification levels at 60 to 70 percent of standards to account for production variability and in-use durability. With greater stress on in-use durability, Tier I vehicle certification levels decreased to about 50 percent at standards. For the LEV certified vehicles, margins are even greater. However, in analyzing the compliance margin associated with LEV certifications, it is important to note the potential for some trade-off in HC and NO_x emissions through calibration adjustments toward richer or leaner A/F ratios. To normalize for potential calibration differences, EEA analyzed the LEV compliance margin in terms of HC plus NO_x emissions. Figure 3-1 shows the distribution of HC+NO_x emissions as a function of test weight for all LEV-certified LDV and LDT families, as well as the ULEV Honda Accord. With one exception (the Ford Ranger), all LDTs are at or above 4000 lbs test weight, while all LDVs are at or below 4000 lbs. Although LDT2 vehicles are certified to a less stringent standard, the data in Figure 3-1 shows no discontinuity in emission levels above 4000 lb test weight.

As can be seen from Figure 3-1, there are wide variations in certification levels, but the certification levels of many LEVs are remarkably low. For example, the HC+NO_x equivalent certification standard for LDVs at 100,000 miles is 0.4 g/mi and the majority of vehicles are less than one-third the standard. In particular, certification NO_x levels are extremely low, with many vehicles at 0.05 to 0.07 g/mi at 100,000 miles, about 20 percent of the certification standard of 0.3 g/mi. It is well known that certification durability requirements are less stringent than in use requirements, but the percent “headroom” has changed relative to Tier I and earlier vehicles. Two of the manufacturers interviewed stated that were concerns on the variability of NO_x emissions and that certification levels may not reflect in-use levels. Other manufacturers suggested that inexperience with LEV standards had led to an overdesign of the catalyst system, and future lower cost systems may not retain this advantage of very low emissions.

Figure 3-1. 1998 LEV Certification HC+NOx Data



The data in Figure 3-1 also suggest that HC+NO_x emissions increase with test weight. We recognize the LDT2 are certified to a different standard which may be reflected in the analysis. A regression analysis revealed the following relationship between HC+NO_x and test weight (TW):

$$\text{HC} + \text{NO}_x \text{ (50K mi)} = -0.051 + \frac{0.054 \text{ (TW/1000)}}{(0.015)^*}$$

$$\text{HC} + \text{NO}_x \text{ (100K mi)} = -0.083 + \frac{0.072 \text{ (TW/1000)}}{(0.018)}$$

Both 50,000 and 100,000 mile certification levels are a statistically significant function of test weight. It is also possible that HC+ NO_x is a function of engine size (CID) as regression analysis showed statistically significant results for this parameter as well:

$$\text{HC} + \text{NO}_x \text{ (50K mi)} = 0.020 + \frac{0.076 \text{ (CID/100)}}{(0.024)}$$

$$\text{HC} + \text{NO}_x \text{ (100K mi)} = 0.002 + \frac{0.107 \text{ (CID/100)}}{(0.029)}$$

However, there is significant multicollinearity between the CID and test weight, so that their separate effects could not be estimated. There is also the issue of multicollinearity with LDT2 standards although visual examination of the data does not suggest this dependence. Engineering analysis suggests that HC emissions should increase with displacement while NO_x emissions should increase with test weight, and a clear separation of effects may be possible as more data becomes available. Due to the multicollinearity effects, the results of the above regressions should be interpreted with caution.

* Values in parenthesis indicate the standard error of the regression coefficients.

3.4 CONTROL OF NO_x EMISSIONS

The NO_x standards prescribed by ARB for LEVs and ULEVs are generally less stringent than the corresponding HC standards; the ratio of NO_x to HC standards is 1.6 for Tier 1 vehicles but is about 2.7 for LEV and 5 for ULEV. EPA is interested in examining alternative ratios that may require further NO_x reduction relative to the California LEV and ULEV standards, possibly at the expense of less stringent HC control.

Section 3.2 discussed the various control technologies available to further reduce the emissions of Tier 1 vehicles, and these technologies have different relative impacts on HC and NO_x. Table 3-2 shows a qualitative assessment of each technology's impact on HC and NO_x, ignoring any synergistic effects of combining technologies. As can be seen from the table, many technologies reduced both NO_x and HC emissions, and these generally represent the technologies that have been introduced in the 1998 LEVs. Such technologies include tighter control of A/F ratio, larger and/or more highly loaded catalysts, and the use of high swirl, high turbulence combustion chambers. As a result, the LEV certification levels for both NO_x and HC are quite low, and the NO_x to HC ratios are at traditional levels of 1.5 to 2. Most LEVs have HC certification emissions in the range of 0.04 to 0.06 g/mi while NO_x levels are from 0.06 to 0.13 g/mi. LEVs with very low emission levels of NO_x include the Mitsubishi Mirage at 0.04 g/mi, the Honda Civic at 0.05 g/mi, the Nissan Altima at 0.05 g/mi, and a TLEV certified Chrysler Cirrus at 0.03 g/mi. These very low levels of NO_x indicate that the rich bias effect has probably been utilized to the point where any additional bias would be counterproductive, resulting in increases in HC+NO_x emissions.

As part of its rulemaking on SFTP emission standards for LEVs, the ARB has utilized arguments suggesting that rich bias has significant benefits in vehicles with certification levels capable of meeting LEV standards,. Most of the testing to support ARB's contention was on the SFTP cycles, and ARB demonstrated a major reduction in HC+NO_x emissions with rich bias. On a sample of 11 cars tested on the US06, the average HC+NO_x declined from 0.255 g/mi to 0.095

Table 3-2. Individual Technology-Specific Impacts on HC and NO_x

Technology	HC Impact	NO _x Impact	Comment
Air-Assisted Atomizers	+	0	Leaner operation may raise NO _x
Tight Control of A/F	++	++	
Reduced Crevice Volume	+	0	
High Swirl/Turbulence Combustion Chamber	+	(+)	NO _x could be affected by increased EGR tolerance
Increased EGR Rate	-	++	May reduce control level of A/F ratio
Rich Bias of A/F	-	+	Negative HC impact only in certain range
Air Injection and Rich A/F Warm-up	+ to ++	0 to +	NO _x influenced by faster warm-up of catalyst
High Cell Density Close-Coupled Catalyst (holding loading constant)	+	~0	HC catalysis affected by surface area
Increased Precious Metal Loading	+ to ++	+ to ++	Pd favors HC and CO reduction
Increased Rh Loading	~0	+	High cost effect

- ++ indicates a greater than 10 percent emissions reduction.
- + indicates a 3 to 10 percent emissions reduction.
- 0 indicates a ± 3 percent emissions effect.
- indicates a 3 to 10 percent emissions increase.

g/mi. However, detailed examination showed that most of the reduction came from three vehicles with abnormally high NO_x emissions (over 5 times the NO_x emissions of the other eight vehicles). Removing these three vehicles from consideration showed that rich biasing caused more typical US06 HC+NO_x emissions to decline from 0.10 g/mi to 0.071 g/mi on average. Over the FTP cycle, the benefits were even more modest. Six vehicles tested on the FTP with and without rich bias showed variable results. Two vehicles showed small increases in HC+NO_x, (6.9 and 8.9 percent), while three others showed small decreases (7.5, 10.1, and 12.2 percent). Only one vehicle (an LDT1) showed a significant decrease in HC+ NO_x of 22 percent. Based on the ARB data and the new 1998 LEV certification data, it appears that most vehicles already have set rich bias to levels close to the HC+NO_x minimum, or are in a zone of indifference and further changes toward additional rich bias would likely cause only small changes to HC+NO_x emissions (either up or down). However, this also implies that HC can be traded for NO_x to some limited degree on a one to one basis, but the extent cannot be determined from the ARB data which tested each vehicle only at 2 points on the bias curve.

EGR is the second of three technologies that can reduce NO_x emissions. Manufacturer inputs suggested that LEV and ULEV EGR rates are not significantly different from Tier 1 vehicles and some manufacturers stated that EGR system complexity need not increase to meet LEV or ULEV standards. This is confirmed from data on current LEVs, where there are no mechanical differences in the EGR systems between the LEVs examined and their Tier 1 counterparts. In fact, while the Tier 1 Honda Civic has EGR, its LEV counterpart does not. Manufacturers stated that EGR impacts the ability to control net A/F ratios tightly due to dynamic changes in exhaust back pressure and temperature, and that the advantages of increasing EGR flow rates are lost partly in losses in A/F ratio control even with electronic control of EGR. Higher EGR flow rates can be tolerated by modern engines with more advanced combustion chambers, but EGR cooling may be necessary to achieve higher EGR flow rates within acceptable detonation limits and without significant loss of A/F control. EEA is of the opinion that using cooled EGR and higher flow rates (in the 20 to 25 percent EGR rate range) can allow for further engine-out NO_x reductions in modern engines in the range of 15 to 25 percent.

The third technology that can reduce NO_x is increasing rhodium (Rh) loadings in the catalyst. Certification data reveals that many LEVs are Pt/Rh catalysts with a ratio of 5:1, although absolute loading levels vary. Some vehicles use close-coupled catalysts of Pd/Pt/Rh type but in these catalysts Pt/Rh loadings are much smaller than Pd loadings, with ratios in the range of 85/12/3. It is possible that increases in rhodium loadings for both Pt/Rh and Pd/Pt/Rh catalysts can further enhance NO_x conversion. However, the effect of rhodium loadings on catalyst NO_x efficiency saturates at relatively low Rh levels according to catalyst manufacturing representatives, so that there may not be much room for improvement in current Pt/Rh catalysts. It is difficult to provide an estimate of how much additional benefit in NO_x control is possible, although some added benefit is likely.

Much of the uncertainty in forecasting levels of possible additional NO_x control is due to the very low certification levels already attained by LEVs. It is not clear if production variability and in-use NO_x deterioration are high enough to merit setting certification NO_x levels so low, but data on this topic may be available over the next year to two from enforcement audits and in-use testing.

Based on the considerations listed above, EEA developed two bundles of technologies for modern design (2-valve or 4-valve) engines, one of which is HC focused per current ARB standards and the second of which is NO_x focused per the preceding discussion. These bundles, as identified in Table 3-3, are used as prototypical bundles for the cost analysis which follows.

3.5 COST OF TECHNOLOGY BUNDLES

The term “cost” has many different meanings depending on the context it is used in, but the retail price equivalent (RPE) is often utilized by the auto-industry as an indicator of the average price impact to consumers. The estimation of the RPE requires a detailed knowledge of the economics of the auto industry. A number of approaches have been developed to best characterize the

Table 3-3. Technology Bundle Definition For Modern Engine Designs

Technology	Included in HC Focused Bundle?	Included in NO _x Focused Bundle?
Air-Assisted Atomizers	Possible *	No
Adaptive Control of A/F Ratio	Yes	Yes
Advanced Planar Oxygen Sensors	Yes	Yes
Reduced Crevice Volume and Low Oil Consumption Design	Yes	No
Secondary Air Injection	Possible	No
Closed-Coupled + Underfloor Catalyst	Yes	Possible
Close-Coupled Catalyst	High Pd	Tri-metal
Cooled EGR at High Rates	No	Yes
High Cell Density Closed-Coupled Catalyst	Yes	No
High Rhodium Underfloor Catalyst	No	Yes

* Possible indicates that the technology may be used in some, but not all, compliant designs.

various cost elements that go into an RPE estimate. In addition, the dynamic nature of the auto industry makes it particularly difficult to establish a single RPE with a high degree of certainty. In developing the methodology summarized below, EEA has built on an RPE methodology developed by Lindgren³ for the EPA. The EEA method to calculate RPE assumes a 20 percent factory overhead and a 20 percent general overhead for administration, sales, marketing, and research and development. The net factory cost is the fully burdened variable cost plus the capital cost amortized over eight years, at a 15 percent rate of return. The RPE also includes a 20 percent markup on factory cost to account for transportation, dealership cost, and marketing. Some manufacturers supplied RPE's and others supplied variable costs. These data were converted to standard costs and prices using the stated methodology.

Some observers state that overhead burdens should not be utilized to estimate RPE, since they believe that the burdens imply increased fixed costs. The methodology described above does **not** imply that fixed costs increase with variable cost increases as commonly misunderstood. Consider the entire industry as a single manufacturer and assume that the emissions control components cause variable costs to increase by \$200, and assume that the average vehicle price is \$20,000. The net increase in vehicle price should be only \$200 if all overhead costs are fixed costs, but this increase in vehicle price will cause sales to decrease slightly. There is much economic evidence to suggest that the elasticity of car sales with respect to price is -0.8 to -1.0, so that the car price increase of one percent will cause car sales to decrease by 0.8 to 1 percent. Since the fixed overhead costs must be covered by fewer vehicles sold, the absolute overhead allocated to each vehicle must increase. It is easy to show that the same overhead multiplier must be applied to all variable costs to maintain the same total absolute overhead when the elasticity is exactly -1.0. In reality, total overhead will increase a little as the new components will increase inventory costs and warranty costs, but this increase may be approximately offset by the fact that elasticity is slightly more than -1.0. Hence, EEA is of the opinion that the overhead multiplier approach is the correct way to determine net price impacts at least to first order, and is identical to the approach used historically by EPA.

This section documents both the variable cost of components and resulting RPE for the technologies required to reduce emissions below Tier 1 levels. Cost data at the component level includes confidential data submitted by the manufacturers to EEA, limited data from suppliers, and data obtained from industry sources in previous studies conducted by EEA for EPA. Since these data are submitted under confidentiality agreements with the respective parties, this section only shows EEA's best estimate of component costs after considering all confidential data in the aggregate. In no case are EEA estimates associated with data provided by any one manufacturer or supplier. For specific components, data obtained from several sources are in good agreement while for certain others, data are quite divergent. The most divergent estimates apply to electronic air pump- based secondary air systems and catalyst costs. In these cases, EEA utilized informal contacts with manufacturers of catalysts and air pumps to select from among the various estimates. We also believe that some of the divergence can be attributed to some manufacturers being more adept at developing low cost ways to reduce emissions. For example, one European manufacturer acknowledged that its current systems for meeting LEV/ULEV standards were very high cost, and not representative of average industry cost.

The cost analysis is not associated with the sales weighted average cost of meeting a standard, since no standard was specified for analysis. Technology costs were estimated for the bundles of technologies described in the previous subsection, starting with a basic bundle that should allow modern engines of up to 4 liters displacement to meet California LDV LEV standards. Costs are then estimated for two additional technology bundles, one a stringent HC control bundle and the second a stringent NO_x control bundle. The first bundle could allow modern engines to meet ULEV standards, but may be required by older design and/or large displacement engines to meet LEV standards. The stringent NO_x control bundle could allow a 30 to 35 percent reduction in NO_x compared to the basic LEV bundle, although associated HC emissions could be up to 10 percent higher. Some engine families may already incorporate one or more of these technologies to meet Tier I and SFTP standards, but the costs derived here are not market weighted incremental costs.

Two significant issues arise in costing these bundles. First, manufacturers can choose among alternative catalyst designs such as a small volume close-coupled plus standard underfloor catalyst, a single larger and more highly loaded catalyst, or a staged series of catalyst beds in one single enclosure. The actual choice will depend on vehicle-specific packaging constraints and engine-out emission levels. The small close-coupled plus underfloor catalyst appears to be the most popular and likely concept, but other designs are likely to be quite similar in total cost. For example, the single large catalyst may be cheaper than the two catalyst system, but may require a heat insulated manifold and exhaust pipe so that total system costs are quite similar. The second issue relates to current versus future costs. Only one manufacturer explicitly addressed the question of future cost reductions and, based on historical experience, suggested that a 30 percent reduction from current costs may be possible by 2004/2005 due to learning, technology evolution, and improved engine design.

Table 3-4 shows the variable cost of the basic bundle of technologies to be \$88 (+\$16 if air-assisted atomizers are used) for a 2.2 liter four cylinder engine. As indicated in Table 3-5, this translates into an RPE of \$173 to \$199. A similar analysis for a 3.5L V-6 shows an RPE of \$261 to \$302. These are near term values; if costs decline by 30 percent in the next 5 to 7 years, the RPE will be \$120 to \$140 for a four cylinder, and \$183 to \$211 for a six cylinder engine. The “stringent HC control” bundle adds an air pump and a duplex loaded* close-coupled catalyst that results in a variable cost increase of \$150 for a four cylinder engine and \$200 for a six cylinder engine. Near term RPE increases by an additional \$257 and \$342 respectively, while long term RPE increases could be \$180 and \$239 for the four cylinder and six cylinder cases. In contrast, the “stringent NO_x control” bundle, which would include full electronic control closed loop EGR with an intercooler, increased rhodium loading, and increased rich bias (a zero cost item) would increase variable cost by \$42 and \$52 and near term RPE by \$74 and \$95 for the four and six cylinder cases respectively. Long term RPE impact would be an additional \$51 and

* Duplex loading indicates loading rates that are double those of the basic technology bundle catalyst.

Table 3-4. Variable Cost of Technology Bundles Relative to Tier 1 Technology
(Incremental cost relative to typical Tier I vehicle, Pre-SFTP standard)

Technology	2.2 L, Four Cylinder	3.5L, Six Cylinder
Air-Assisted Atomizers (Optional)	(\$16)*	(\$24)
Improved A/F Control Hardware (Fast Response Injectors, faster microprocessor)	\$3	\$5
Planar Oxygen Sensors	\$4	\$8
Close-coupled Catalyst	\$55	\$90
Washcoat/Substrate Improvement	\$10	\$15
Piston Top Land Height	\$4	\$6
Underhood Heat Management	\$12	\$16
BASIC BUNDLE VARIABLE COST	\$88(+ \$16)	\$140(+ \$24)
Potential Long Term Variable Cost	\$66 (+12)	\$105 (+18)
Additional Cost of “Stringent HC Control” Bundle		
Electric Air Pump System	\$125	\$160
Duplex Loaded Catalyst	\$25	\$40
STRINGENT HC BUNDLE COST	\$150	\$200
Potential Long Term Variable Cost	\$110	\$150
Additional Cost of “Stringent NO_x Control” Bundle		
Full Electronic Control Closed Loop EGR	\$17	\$17
EGR Cooling	\$15	\$20
Increased Rhodium Loading	\$10	\$16
STRINGENT NO_x BUNDLE COST	\$42	\$53
Potential Long Term Variable Cost	\$31.50	\$40

* Parenthesis are used to indicate optional (not negative) costs.

Note: These costs are incremental costs only relative to an average LDV with a modern OHV engine, calibrated to Tier I standards. Costs for all possible engine designs were not investigated

Table 3-5. Incremental Retail Price Equivalent of Technology Bundles

2.2L, Four Cylinder Engine	Basic Bundle	Stringent HC Control Bundle	Stringent NO_x Control Bundle
Variable Cost	\$88 (+\$16)*	\$150	\$42
Factory Overhead	\$18 (+\$3)	30	8
Corporate Overhead	\$18 (+\$3)	30	8
Engineering and Tooling Amortization	\$20	4	4
Dealer and Marketing Cost	\$29 (+\$4)	\$43	\$12
NEAR TERM RPE	\$173 to \$199	\$257	\$74
POTENTIAL LONG TERM RPE	\$120 to \$140	\$180	\$52
3.5L, Six Cylinder Engine	Basic Bundle	Stringent HC Control Bundle	Stringent NO_x Control Bundle
Variable Cost	\$140 (+\$24)	\$200	\$53
Factory Overhead	\$28 (+\$5)	\$40	\$11
Corporate Overhead	\$28 (+\$5)	\$40	\$10
Engineering and Tooling Amortization	\$22	\$5	\$5
Dealer and Marketing Cost	\$43 (+\$7)	\$57	\$16
NEAR TERM RPE	\$261 to \$302	\$342	\$95
POTENTIAL LONG TERM RPE	\$183 to \$211	\$239	\$67

* Parenthesis are used to indicate optional (not negative) costs.

\$67 respectively. Costs for other engine sizes can be computed by scaling the catalyst costs and cylinder-specific costs of pistons/injectors. It should be noted that some of these costs, especially costs for catalysts and heat shielding, may not be incremental to the costs of meeting the SFTP requirements which are not included in the analysis for this report. Moreover, some cars already feature these technologies to some limited extent, so that the costs are not the incremental costs of meeting a specific standard.

A comparison of component costs and total RPE with published estimates from ARB is also instructive. Table 3-6 presents a comparison between EEA's manufacturer derived estimates and ARB cost estimates. The largest cost differences are for the air pump, although ARB's, estimates are typically lower than EEA's for most technologies, and may reflect long run cost (for which EEA estimates a 25 percent reduction over current costs). However, RPEs are very different because ARB does not account for fixed cost burdens that EEA has listed in Table 3-6, for reasons explained in the paragraphs above.

3.6 REFERENCES

1. Energy and Environmental Analysis, Inc., "Emission Control Technology Distribution, Final Report", prepared for the U.S. Environmental Protection Agency, February 10, 1997.
2. Energy and Environmental Analysis, Inc., "Assessment of Technology Costs to Comply with Proposed FTP Revisions", prepared for the U.S. Environmental Protection Agency, September 1995.
3. Lindgren, L "Cost Estimation for Emission Control Related Components/Systems and Cost Methodology" EPA Report No. 460/3-78-002, 1978.

**Table 3-6. Variable Cost Comparison: ARB Estimates
Versus EEA Estimates**

	4-Cylinder		6-Cylinder	
	EEA	ARB	EEA	ARB
Air Assisted Atomizers	16	8	24	12
Improved A/F Control	3	0	5	0
(Planar EGO)/UEGO	4	10	8	20
Insulated Exhaust	NE	1	NE	4
Greater Catalyst Loading	25*	0*	25*	0*
Close Coupled Catalyst	55	55	90	55
Improved Washcoat	10	0	15	0
Piston Top Land Height/ Engine Modification	4	0	6	10
Electric Air Pump	125	50	160	50
Full Electronic EGR	17	10	17	20
Underhood Heat Management	12	NE	16	NE

NE - Not estimated

* May not refer to same technology, ARB assumes Pd catalyst cost will offset increases in loading.

4. SULFUR TOLERANCE

4.1 OVERVIEW

With the advent of onboard diagnostic system (OBD II) requirements and the introduction of advanced technology vehicles, the issue of exhaust sulfur impacts on vehicle emission control system performance has received much recent attention. While this attention has been driven by the potential negative impacts of sulfur on both advanced technology vehicle emissions and the integrity of OBD II malfunction decision making, the issue of fuel sulfur on vehicle emissions performance is not new. In the automotive field, sulfur was recognized as a vehicle catalyst poison during the initial stages of oxidation catalyst development in the early-1970's and considerable research on the magnitude of sulfur impacts on catalyst performance took place during the early years of three-way catalyst development in the mid-to-late 1970's.¹⁻⁷ The negative role of sulfur on the performance of non-automotive catalysts in a variety of applications, such as hydrogenation, hydrocracking, and catalytic reforming, has been recognized for an even longer period. Sulfur impacts on vehicle emissions performance are not limited to the poisoning of automotive catalysts. Exhaust gas oxygen sensors rely on similar catalytic principles and, therefore, can also be affected by exhaust sulfur levels.

Sulfur in automotive exhaust is a direct function of fuel sulfur levels. While sulfur has no intrinsic value in automotive fuel, it is present as an impurity in crude oil. Several refinery processes remove sulfur from crude oil during processing (e.g., hydrotreating to pretreat reforming feedstreams) and such "low sulfur" processing has become more prevalent to facilitate the production of fuels from lower quality crude oils, but significant sulfur can remain in final fuel blends. Specific fuel sulfur levels vary in accordance with crude oil quality and refining practices (at the individual refinery level), but levels in commercial gasoline throughout the U.S. generally range from 50 to 600 parts per million

by weight (ppmW), although higher concentrations can be observed. Diesel fuel sulfur levels have historically been higher than those of gasoline, averaging 2500 ppmW or more prior to 1993. Since late 1993, on-road diesel fuel sulfur content has been limited to 500 ppmW by the EPA to reduce SO₂ and particulate sulfate emissions as well as facilitate the introduction of oxidation catalysts and particulate traps on heavy duty diesel vehicles.⁸

Conceptually, the impact of sulfur on vehicle emissions performance can be likened to that of lead which, when present in automotive exhaust, effectively undergoes strong interaction with the noble metals used in oxidation and three-way catalysts, reducing conversion efficiency and increasing tailpipe emissions. However, unlike sulfur which is present as an impurity in crude oil, lead is not an artifact of crude oil processing, but rather was blended into automotive gasoline for its octane enhancing and engine lubrication properties. Achieving these same properties through alternative mechanisms (e.g., hardened engine valves, greater use of aromatics in gasoline formulation) allowed the practice of lead blending to be curtailed and the introduction of unleaded gasoline to take place in conjunction with the introduction of the automotive catalytic converter. By comparison, a similar reduction in fuel sulfur content would require additional crude processing steps (i.e., hydrotreating), using equipment not found at all refineries or, when present, not sufficiently sized to handle all gasoline production. Therefore, efforts to control fuel sulfur content would require substantial capital investment by petroleum refiners.

4.2 FUEL SULFUR LIMITS

There are no national regulatory limits on the sulfur content of gasoline currently sold in the U.S. However, the ASTM (American Society for Testing and Materials) D4814 standard for automotive gasoline, generally recognized and adhered to by U.S. gasoline producers on a voluntary basis, includes a maximum sulfur limit of 1000 ppmW for unleaded gasoline.⁹ This ASTM sulfur limit has been in place throughout the period of vehicle emissions regulation (under ASTM D439¹⁰ before the adoption of D4814), but its establishment was not intended to

(directly) affect the environmental performance of vehicles. Its stated design purpose is to limit engine wear, lubrication oil deterioration, and exhaust system corrosion.

National regulations are in affect, which will limit the sulfur content of some U.S. gasoline beginning in the year 1998. Under the EPA's Federal Reformulated Gasoline (FedRFG) program, producers of FedRFG are required to demonstrate compliance with program requirements using the FedRFG Complex Model at that time. Since the Complex Model restricts allowable FedRFG sulfur content to 500 ppmW, areas subject to the program will be subject to an effective sulfur limit of 500 ppmW beginning in 1998.¹¹ It should also be noted that, although the allowable sulfur limit will remain at 500 ppmW, the actual sulfur content of gasoline sold in areas subject to the FedRFG program after 1999 is expected to be less than 200 ppmW to facilitate compliance with the NO_x reduction requirements of Phase II of the FedRFG program. Conventional gasoline with sulfur contents as high as 1000 ppmW will continue to be allowed in areas not subject to the FedRFG program. Generally, FedRFG is required to be sold in those U.S. areas with the poorest tropospheric ozone-related air quality.

At the state level, the sulfur content of unleaded gasoline has been regulated in California since 1976, at which time a cap of 500 ppmW was imposed. The cap declined to 400 ppmW in 1978 and 300 ppmW in 1980, remaining at that level through 1996. These limits were imposed in California in response to concerns over elevated sulfate emissions from catalyst-equipped vehicles.¹² During 1996, California imposed even more stringent sulfur limits on automotive gasoline as an integral component of the California Reformulated Gasoline (CaRFG) program. Under the CaRFG program, fuel providers in the State can either meet a flat limit of 40 ppmW or an average limit of 30 ppmW in conjunction with a cap of 80 ppmW. Therefore, no gasoline sold in California today can have a sulfur content in excess of 80 ppmW. Unlike the predecessor sulfur limits which targeted sulfate emissions, CaRFG limits are specifically designed to maximize the efficiency of automotive three-way catalytic converters.¹³

As alluded to in Section 4.1, the sulfur content of on-road diesel fuel throughout the U.S. has been limited to 500 ppmW since October 1, 1993.⁸ This limitation was imposed by the EPA to reduce engine wear and secondary particulate formation as well as facilitate heavy duty diesel engine manufacturer compliance with stringent particulate matter emission standards implemented beginning in the early 1990's. An equivalent diesel fuel sulfur limit (i.e., 500 ppmW) was imposed statewide in California at the same time as a component of that State's Reformulated Diesel Fuel (Clean Diesel) program.¹² Prior to that time, the only national limits on on-road diesel fuel sulfur content were the voluntary limits established under the ASTM D975 standard.¹⁴ For automotive applications, ASTM D975 limited diesel fuel sulfur content to 5000 ppmW. In California, a diesel fuel sulfur limit of 500 ppmW was put in effect in the Los Angeles area as early as 1985 (for large refiners, small refiners were exempt until 1989), but the limit for the rest of the State was maintained at the ASTM recommended value of 5000 ppmW until the Clean Diesel program went into effect in 1993.

Outside the U.S., movement toward lower sulfur motor vehicle fuel is underway.^{15,16} In Japan, the sulfur content of gasoline is currently limited to 100 ppmW. In Europe, on-road diesel fuel is currently limited to 500 ppmW sulfur, while a very low sulfur (less than 10 ppmW) "City Diesel" fuel is available in several metropolitan areas. Gasoline sulfur content in Europe is the subject of current debate, with proposed limits ranging from 30-200 ppmW for the 2000 timeframe and 30-50 ppmW by 2005. Similar levels of control for diesel fuel are also under consideration.

4.3 SULFUR IMPACTS ON EMISSIONS CONTROL SYSTEM PERFORMANCE

Engine-out emissions have been shown to be relatively independent of fuel sulfur content.¹⁷⁻¹⁹ Therefore, fuel sulfur content was of little concern prior to the widespread use of post-combustion emission control devices (i.e., catalytic converters) on motor vehicles beginning in the early 1970's. The catalyst poisoning potential of fuel sulfur (or more accurately of SO₂, the primary exhaust component associated with the combustion of fuel sulfur) was recognized

during the development stages of the first generation of automotive catalysts, but this potential was not of great concern due to the oxidizing-only nature of automotive catalysts at that time.^{2,4-6} In an oxidizing environment, SO_2 is rapidly converted to SO_3 , which has a much lower catalyst poisoning potential. Therefore, serious concern over the poisoning potential of fuel sulfur was not evidenced until the introduction of three-way automotive catalysts in the late 1970's.

Despite the non-urgency of catalyst poisoning effects during the oxidation catalyst era of the 1970's, fuel sulfur was, interestingly, of significant concern due to the potential for sulfuric acid formation in the same oxidizing environments of those catalysts.²⁰⁻²⁷ As indicated above, exhaust SO_2 is converted to SO_3 in the excess air operating environments commonly associated with early oxidation catalysts. SO_3 can subsequently react with water, either in the exhaust system or in the atmosphere to form sulfuric acid which is of concern, both for its direct health impacts and its tendency to form particulate sulfate during subsequent neutralization reactions. While the overall level of sulfuric acid emissions from gasoline vehicles was never viewed as significant relative to stationary source SO_2 emissions, the potential for localized problems in areas of high traffic density was considered to be potentially significant and considerable associated research was undertaken to minimize the sulfuric acid potential of oxidation catalysts.

With the advent of stringent NO_x standards in the late 1970's, automotive catalyst development efforts were shifted toward three-way converters capable of simultaneously oxidizing HC and CO and reducing NO_x in a stoichiometric or near-stoichiometric environment. With this shift, concern over the poisoning effects of sulfur on converter performance became widespread and considerable research was undertaken to quantify and understand the poisoning mechanisms.¹⁻⁷ While no formal actions were undertaken at that time to either limit fuel sulfur or develop an alternative long term response, efforts to reduce catalyst sensitivity to sulfur were undertaken by automotive catalyst manufacturers, including the introduction of nickel into catalyst formulations as a sulfur scavenging agent. A number of reasons exist for the apparent lack of definitive response during the early years of three-way automotive catalysis, including: (1) sometimes

conflicting research estimates of both the magnitude and the reversibility of the sulfur poisoning effect, (2) the relative primitiveness of automotive three-way catalysis at the time, where net conversion rates of 60-80 percent were common, and (3) the utility of an emissions standard certification fuel (indolene) with a sulfur content generally below 100 ppmW* (allowing auto manufacturers to be isolated to a large degree from in-use sulfur impacts on vehicle emissions).

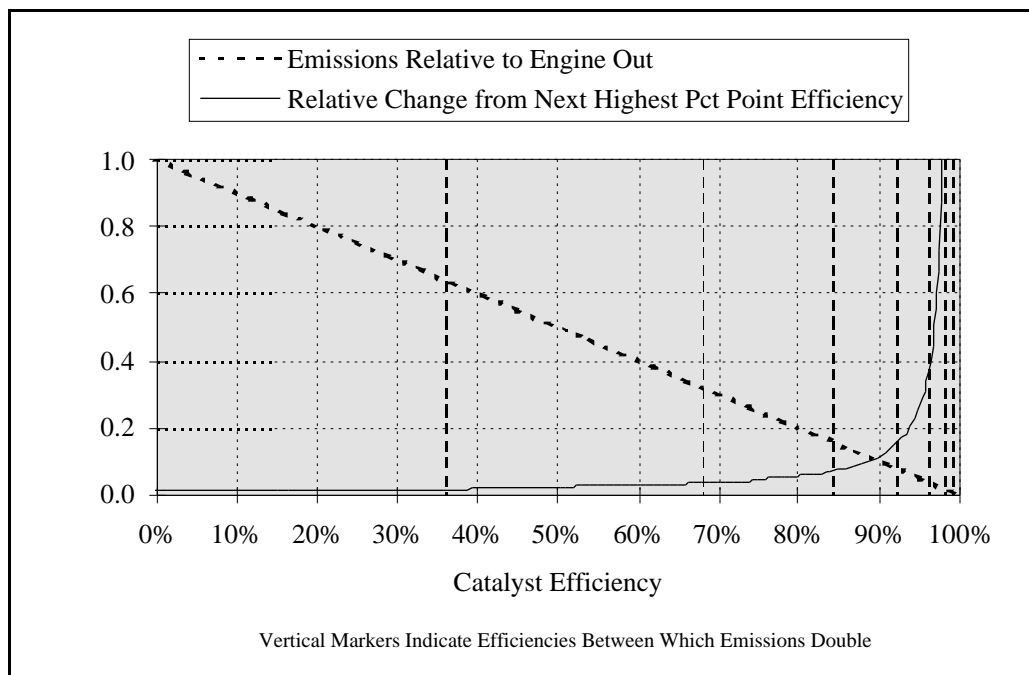
Today's three-way catalysts are substantially more complex than those of the late 1970's and early 1980's. In addition to platinum, palladium, and rhodium noble metals, current three-way catalysts include a number of base metal and rare earth oxides (of, for example, cerium, lanthanum, nickel, barium, iron, and neodymium) and are formulated for very high conversion efficiencies with extended thermal and mechanical durability. The high performance levels of these catalysts has enabled auto manufacturers to meet very stringent emission standards including, in some cases, the California Low Emissions Vehicle (LEV) and Ultra-Low Emissions Vehicle (ULEV) standards. To meet these very low emissions levels, automotive catalysts are expected to maintain conversion efficiencies of 90 percent or better for HC and NO_x and 80 percent or better for CO, with very little in-use deterioration. For ULEV-stringency standards, catalyst efficiencies of over 90 percent for CO and NO_x and approaching 100 percent for HC are required (barring any substantial reduction in engine-out emissions). For example, to achieve ULEV standards with a 25 percent compliance margin, efficient engine-out emission rates of 1.5 grams per mile (g/mi) for HC, 15 g/mi for CO, and 1.5 g/mi for NO_x, post-combustion oxidation/reduction efficiencies of at least 98 percent for HC, 92 percent for CO, and 90 percent for NO_x must be maintained for 50,000 miles.

To better understand the significance of such high post-combustion conversion efficiencies and the sensitivity of tailpipe emissions to even small deviations in these efficiencies, a simple

* Analysis of laboratory test results for 42 batches of indolene purchased by the U.S. EPA's Office of Mobile Sources in Ann Arbor, Michigan between 1977 and 1996 indicates an average sulfur content of 66 ppmW.

examination of the relationship between engine-out and tailpipe emissions is helpful. Figure 4-1a graphically presents the critical elements of this relationship. The downward sloping diagonal represents the ratio of tailpipe emissions to engine-out emissions for increasing conversion efficiencies and illustrates the obvious linear relationship between absolute tailpipe emissions and conversion efficiency. The positive exponential function illustrates the somewhat less obvious ratio between tailpipe emissions at a specific conversion efficiency and tailpipe emissions at a higher conversion efficiency. In this case, the trend line compares the ratio of tailpipe emissions for the plotted efficiency to the tailpipe emissions for the next highest integer value conversion efficiency. Figure 4-1b expands the 85-100 percent efficiency range to provide for a more precise view of trends in this high efficiency range. Both figures include a series of vertical markers which indicate the ranges between which tailpipe emissions double for cumulative losses in conversion efficiency.

Figure 4-1a. Relationship Between Tailpipe Emissions and Catalyst Efficiency



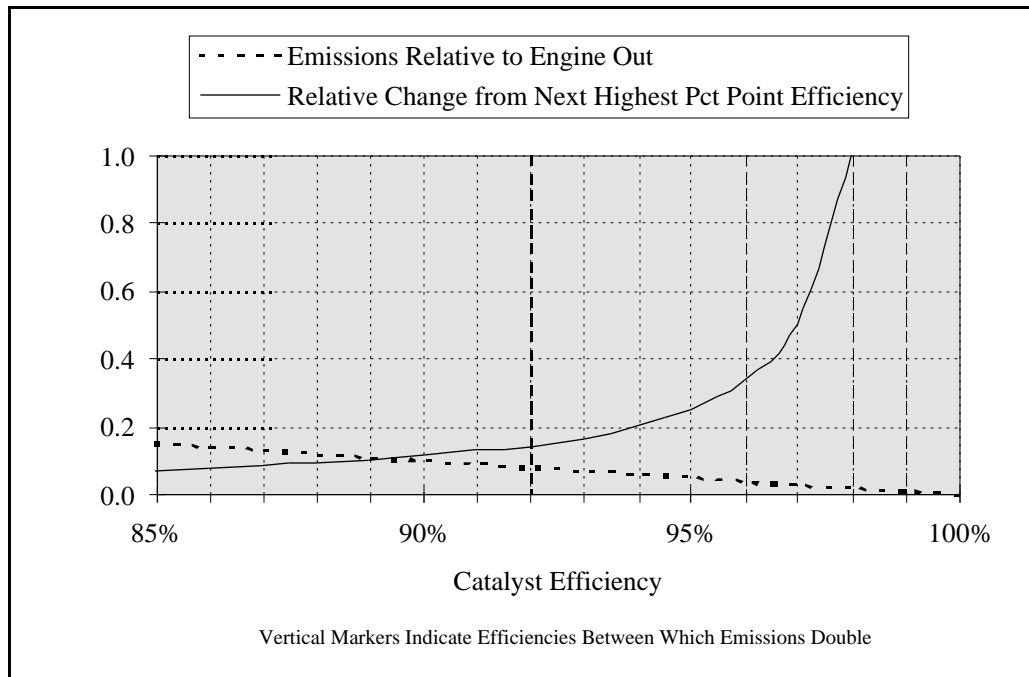


Figure 4-1b. Relationship Between Tailpipe Emissions and Catalyst Efficiency

From Figure 4-1b, it can easily be seen that as little as a one percentage point loss in catalyst efficiency can double tailpipe emissions, if that loss represents a drop from 99 percent to 98 percent efficiency. As illustrated, this relative change in tailpipe emissions decreases rapidly, becoming much less significant when comparing conversion efficiencies of less than 90 percent or so. While the absolute emissions difference of a one percentage point loss in conversion efficiency is no different whether that loss occurs between 98 and 99 percent efficiency or between 10 and 11 percent efficiency, the relative losses differ by nearly two orders of magnitude. An order of magnitude differential exists even between high-90 percent efficiency losses and losses in the 70-80 percent efficiency range. As indicated by the vertical markers, tailpipe emissions will double a full four times for conversion efficiency losses from 99 to 84 percent (once between 99 and 98 percent efficiency, once between 98 and 96 percent efficiency, once between 96 and 92 percent efficiency, and once between 92 and 84 percent efficiency) and

only twice more throughout the full range of possible efficiencies (once between 84 and 68 percent efficiency and once more between 68 and 36 percent efficiency). This obviously excludes any impacts of losses in efficiency above 99 percent, where even greater orders of magnitude changes occur over very small efficiency ranges. The significance of these relationships can be easily understood if one considers that this relative change for just a one percentage point loss in conversion efficiency can be as large or larger than the entire certification standard compliance margin for a vehicle if that certification relies on high post-combustion conversion efficiencies (such as will be necessary for LEV- and ULEV-type certifications).

Given the relationship between potential losses in conversion efficiency and certification compliance margins for high conversion efficiency certifications, it is obvious that the potential impact of fuel sulfur on relative tailpipe emissions is much more significant for today's high conversion catalysts than was the case for the 60-80 percent efficient catalysts of the late-1970's and early 1980's. Therefore, while sulfur impacts were recognized and considerable sulfur research was performed during that period, the "risk" associated with sulfur-driven efficiency loss during that time was considerably reduced from a certification compliance standpoint. Again, the absolute emissions differentials have not changed over the period in any way (for a constant engine-out emissions scenario).

For engine-out HC emissions of 1.5 g/mi, each one percentage point change in conversion efficiency equates to 0.015 g/mi and, therefore, not only is a 97.3 percent efficient conversion required to meet the ULEV HC standard (with no compliance margin), but each one percentage point loss in efficiency generates an emissions increase that is 40 percent as large as the standard itself. Therefore, in no case could a post-combustion conversion efficiency loss of more than 2.5 percentage points be accommodated, regardless of the certification compliance margin. Conversely, only about a 75 percent conversion efficiency would be required for the same vehicle to meet the 1981-1993 "Tier 0" HC standard, and each percentage point loss in efficiency

generates an absolute emissions increase that is 4 percent of the standard. The increased risk of conversion efficiency loss is obvious and accounts for much of the renewed efforts toward understanding and responding to the issue of fuel sulfur effects on emission control system performance.

In addition to the sensitivity of emissions standard compliance to small losses in catalyst efficiency, several additional factors are also contributing to the renewed interest in exhaust sulfur impacts. Auto manufacturers must now install onboard devices to monitor catalyst performance during customer use (i.e., OBD II). OBD II sensors must be capable of alerting both the vehicle owner (through a malfunction indicator light) and vehicle inspection personnel (through onboard fault code storage) of losses in catalyst efficiency. Additionally, various regulatory agencies are investigating (or have investigated) mandatory low emissions fuel formulations, including research into the effects of changes in sulfur content. Finally, emerging technologies such as NO_x adsorbers designed to facilitate high efficiency, low emissions lean-burn combustion have been shown to be very sensitive to exhaust sulfur. Combined, these factors have stimulated significant sulfur effects research over the last several years, most of which is ongoing at this time.*

4.3.1 Catalyst Effects

Research performed under the Auto/Oil Air Quality Improvement Research Program (AQIRP) represents the initial stimulus for much of the renewed interest in the effects of fuel sulfur on vehicle emissions. The AQIRP, conducted between 1989 and 1993, was established to “provide data to help legislators and regulators achieve the nation’s clean air goals.”²⁸ Early AQIRP work indicating significant catalyst efficiency losses for HC, CO, and NO_x with increasing fuel sulfur

* Among the ongoing formal research are a joint program of the American Automobile Manufacturers Association (AAMA) and the Association of International Automobile Manufacturers (AIAM) and programs sponsored by the Coordinating Research Council (CRC) and the American Petroleum Institute (API). The results of these programs, when available, could add substantial new information of the effects of sulfur on the emissions performance of advanced technology vehicles.

content was utilized by the California Air Resources Board to support that States' reformulated gasoline program specifications.^{13,18} In fact, California implemented the most stringent gasoline sulfur limits in the world on the basis of AQIRP research.

While the AQIRP research quantified the overall effect on vehicle emissions performance, it stopped short of investigating either the mechanism of catalyst deactivation or the sensitivity of observed deactivation to catalyst formulation. Subsequent to the AQIRP work, numerous researchers have investigated these issues and a review of their findings provides insight into important issues such as whether advanced catalyst formulations are becoming more or less sulfur "tolerant" and whether there is a reasonable near-term expectation for the development of a sulfur tolerant catalyst.

It should be noted that the information presented in this section is by no means exhaustive. While the basic mechanisms of catalyst sulfur deactivation are understood, there remains significant disagreement over the affect of this deactivation on tailpipe emissions performance over both the Federal Test Procedure (FTP) and during customer use. This disagreement is due to differences inherent in the various sulfur studies undertaken to date, differences which include variable engine control strategies and variable catalyst designs and formulations, each of which can contribute to differences in FTP or in-use emissions performance independent of fuel sulfur. For example, a vehicle with "excess" conversion capacity (through, for example, catalyst "over-design" at typical FTP or in-use operating conditions) could exhibit a tolerance for sulfur over certain operating cycles which exceeds that of a system sized to "just meet" test criteria. EEA does not view the "sacrifice" of excess conversion capacity as true sulfur tolerance for two reasons: (1) sulfur poisoning still occurs in such systems, they simply have sufficient additional capacity to mask some of the poisoning effect and (2) a cheaper design could be implemented

which produces similar emissions performance at lower fuel sulfur levels. Since it is not possible to determine the degree of over-design which may be present in the various sulfur studies performed to date, this section focuses on the deactivation mechanisms which have been widely observed and are generally agreed upon (as determined through a review of recent studies²⁹⁻⁴³). The figures presented below, which have been extracted from various research papers, are intended to provide illustrative examples of the effects discussed, but the magnitude of the observed effects will vary across vehicles in accordance with engine- and aftertreatment-specific design elements.

The basic catalyst deactivation mechanisms of sulfur are widely recognized and fairly well understood on a conceptual basis. Sulfur (as SO₂) can interact with both the precious metals and base metal oxides used in automotive catalysts. Although the primary sulfur combustion product shifts to hydrogen sulfide (H₂S) under rich conditions, this compound displays similar precious metal poisoning properties. SO₂ (or H₂S) adsorbs and dissociates into elemental sulfur and oxygen (or hydrogen) on the surface of precious metals. This adsorbed sulfur impacts catalyst activity both through mechanical blockage of active conversion sites and electronic blockage of neighboring sites, so that its influence on active site availability is much greater than would be the case if sulfur effects were manifested through mechanical blockage alone. In addition to reducing the overall catalyzing activity of the precious metals, sulfur adsorption also increases catalyst light-off temperature (using as the definition of light-off temperature, that temperature at which 50 percent HC conversion is observed). Finally, it has been demonstrated that catalyst activity can be restored to pre-poisoned levels under high temperature operating conditions (after the removal of high sulfur feedgas), but that the required temperature gradients are not commonly encountered during vehicle operation.

In addition to the effective blockage of active conversion sites through precious metal interaction, SO₂ also undergoes a strong reaction with catalyst washcoat components such as cerium oxide, to form sulfates and sulfites. Advanced automotive catalysts rely on cerium oxides to provide an

oxygen storage function, allowing for high efficiency conversion (both oxidation and reduction reactions) in an operating environment that is continually cycling about stoichiometry. In effect, cerium oxides store oxygen under lean conditions (through the reaction of cerium (III) oxide and molecular oxygen to form cerium (IV) oxide) and release this bound oxygen under rich conditions (through the reaction of cerium (IV) oxide with carbon monoxide to form cerium (III) oxide and carbon dioxide). Unless inhibited, the cycling of the cerium oxide storage and release mechanism, in conjunction with air/fuel ratio cycling about stoichiometry, allows the catalyst to function as though engine operation was continuously near stoichiometric.

SO₂ readily reacts with cerium (IV) oxide to form sulfates, reducing both the quantity of stored oxygen available for carbon monoxide oxidation and the quantity of cerium (III) oxide available for subsequent oxygen storage. Cerium sulfate reactions are favored at both high (>500°C) and low (<200°C) temperatures. SO₂ also reacts with the aluminum oxides and alkaline earth promoters used in catalyst washcoats. Given the need for oxygen, all sulfate reactions are favored under net lean or stoichiometric conditions.

Figure 4-2 illustrates the combined effects of precious metal deactivation and washcoat interactions for a LEV technology catalyst. This figure is based on data presented by Gandhi of Ford Motor Company.³² The specific catalyst on which the effects presented are based is a Pd-only formulation with a loading of 110 g/ft³ aged to the equivalent of 100,000 miles. While the absolute magnitude of the indicated effects might vary somewhat across applications in accordance with specific engine designs and catalyst formulations, the indicated trends are generally consistent with the work of most researchers.^{29-31,33-43} For example, Gerry of BP Oil reported efficiency losses for an increase in fuel sulfur from 35 to 300 ppmW of approximately 2 percentage points for HC, 4-10 percentage points for CO, and 2-20 percentage points for NO_x.³³ Robota and Williamson of ASEC Manufacturing report efficiency losses (for various catalyst formulations with LEV-loadings) that are directionally similar but of lesser magnitude, as indicated in Table 4-1.⁴² Clearly, researchers across the entire range of affected industries

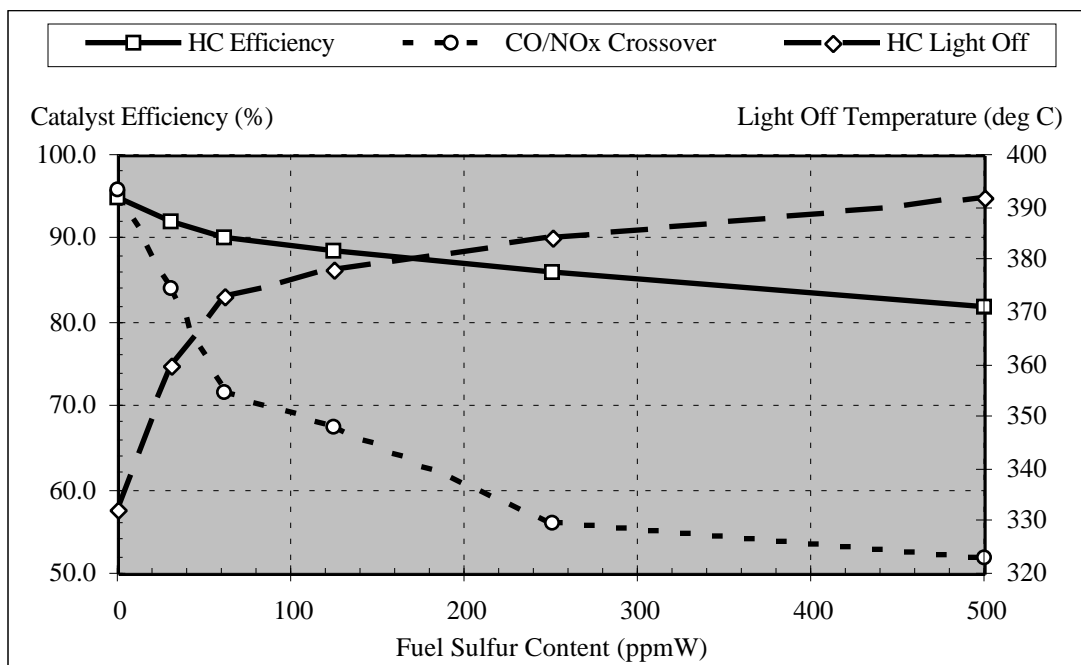


Figure 4-2. Effect of Sulfur on LEV Catalyst Performance³²

Catalyst Type	Loading (g/ft ³)	Pt/Pd/Rh Ratio	NMHC Efficiency Loss (Pct Points)	NO _x Efficiency Loss (Pct Points)
Pd Only	100	n/a	2.4	11.0
Tri-Metal	100	1/10/1	2.7	2.5
Pd/Rh	110	0/10/1	1.8	2.5
Pd/Rh	120	0/11/1	0.8	4.5

Table 4-1. Effect of Increasing Fuel Sulfur from 25 ppmW to 600 ppmW⁴²

(automotive, fuel, and catalyst production) have observed similar indications of decreasing catalyst activity with increases in fuel sulfur. However, equally as clearly, the magnitude of reported effects can vary across applications.

Closer examination of Figure 4-2 and Table 4-1 reveals several specific insights and concerns related to sulfur-driven catalyst deactivation. First, the effects reported by Gandhi raise serious concerns over whether there is any level of fuel sulfur below which catalyst deactivation effects are not evidenced. As shown in Figure 4-2, the greatest rate of catalyst deactivation occurs across fuels with very low sulfur contents, generally in the 0-100 ppmW range. Moreover, we note that catalyst activity increases most quickly as fuel sulfur content approaches zero. Even at the sulfur levels of CaRFG (30-80 ppmW), significant deactivation is evidenced relative to zero sulfur fuel. While the magnitude of this effect might be attributed to the Pd-only formulation of the catalyst tested (Pd-only catalysts have been shown to be more sensitive to fuel sulfur than either dual- or tri-metal catalysts), Gandhi finds similarly shaped deactivation curves for both Pd-only and Pd/Rh formulations. Moreover, Gerry shows similarly shaped curves for Pt/Rh formulations. Therefore, while specific catalyst formulations may be more, or less, sensitive than others, it appears that the greatest fuel sulfur effects occur at very low sulfur levels. Gandhi also performed several additional sensitivity analyses, finding that while both catalyst aging and precious metal loading can influence the overall level of catalyst activity under both poisoning and non-poisoning conditions, the general shape of the deactivation curve does not change.

The work of Robota and Williamson (see Table 4-2) illustrates the sensitivity of the magnitude of sulfur-driven deactivation to catalyst formulation. The catalysts tested all represent currently available commercial formulations with LEV-type loadings, but clearly the Pd-only formulation is more sensitive to sulfur than either the Pd/Rh or tri-metal formulation, with NO_x conversion efficiencies showing the greatest sensitivity regardless of formulation. Bennett, Cooper, and Garr reach similar conclusions on the significance of NO_x sensitivity.^{40,41} The reported effects for the two Pd/Rh formulations tested by Robota and Williamson illustrate the potential tradeoffs in HC

versus NO_x sulfur sensitivity which can be “programmed” into catalyst formulations. The 11/1 Pd/Rh formulation, tailored to favor high HC conversion, exhibits a substantially lower sulfur sensitivity for HC conversion than the more HC/NO_x balanced 10/1 Pd/Rh formulation, but also exhibits nearly twice the sulfur sensitivity for NO_x conversion.

A significant portion of the difference in sulfur sensitivity observed across applications and research programs (including those used to produce Figure 4-2 and Table 4-1 above) may be due to catalyst mounting location (or laboratory test conditions). It is generally agreed that the sulfur deactivation effects on precious metals decrease with increasing catalyst bed temperatures and sulfur deposited on active catalyst sites can be removed at temperatures above 600°C under lean conditions or 700°C under rich conditions. Higher temperatures are required to fully inhibit sulfur base metal and rare earth oxide reactions. Therefore, research performed on extreme close coupled catalysts or under higher temperature laboratory conditions is likely to reflect lower sulfur sensitivities than research performed in more moderate test environments. This is consistent with the data presented in Figures 4-2 and Table 4-1, as Gandhi tested at catalyst inlet temperatures of 500°C, while all catalysts tested by Robota and Williamson were manifold mounted and exhibited inlet temperatures generally ranging from 500°C-650°C.

Figure 4-2 also illustrates the effects of sulfur-induced poisoning on catalyst light-off. As indicated, the temperature required to achieve 50 percent HC conversion efficiency increases by approximately 60°C as fuel sulfur increases from 0 to 500 ppmW. As was the case with overall catalyst deactivation effects, the greatest impact occurs at very low sulfur levels with approximately two-thirds of the overall light-off temperature increase occurring as sulfur levels increase from 0 to only 60 ppmW. Therefore, substantial light-off impact would still be evidenced for fuel sulfur levels as low as those of CaRFG. Like overall sulfur deactivation, the magnitude of light-off impacts will vary across applications and with catalyst formulation.

Figure 4-2 and Table 4-1 illustrate the combined impacts of fuel sulfur on overall catalyst conversion efficiency. As described above, catalyst deactivation is a function of both precious metal and base metal/rare earth oxide interactions with exhaust sulfur. Advanced catalysts are typically formulated to provide significant oxygen storage capacity and the washcoat components which provide this capacity are very sensitive to sulfate formation. Figure 4-3 illustrates the sensitivity of the oxygen storage capacity of two LEV-type catalysts to fuel sulfur (as reported by Beck³⁴ and Gandhi³²). To facilitate comparison across studies using catalysts of varying oxygen storage capacity, the values presented in Figure 4-3 have been normalized so that the oxygen storage capacity with a 300 ppmW sulfur fuel is set to unity (the selection of 300 ppmW is arbitrary and simply reflects a fuel sulfur level common to both studies presented). Although Gandhi finds a somewhat greater poisoning potential than Beck, we note that the effects are fairly consistent and that, once again, significant “deactivation” (i.e., loss of oxygen storage capacity) is observed at very low sulfur levels, with the greatest rate of sulfur-driven deactivation occurring between 0 and 100 ppmW. This is consistent with the relationship described above for overall catalyst deactivation.

4.3.2 Oxygen Sensor Effects

Exhaust gas oxygen (EGO) sensors generally make use of porous platinum as the electrode material between which the ambient/exhaust partial pressure differential of oxygen is determined. Platinum catalysis is a critical element of EGO sensor design, relied upon to establish exhaust gas equilibrium. Due to this reliance on platinum, EGO sensors are subject to the same precious metal deactivation mechanisms associated with sulfur poisoning, as described in Section 4.3.1 above. Moreover, as was also the case with catalytic converter deactivation, the magnitude of EGO sensor sulfur impacts is application specific and can vary with factors such as sensor location.

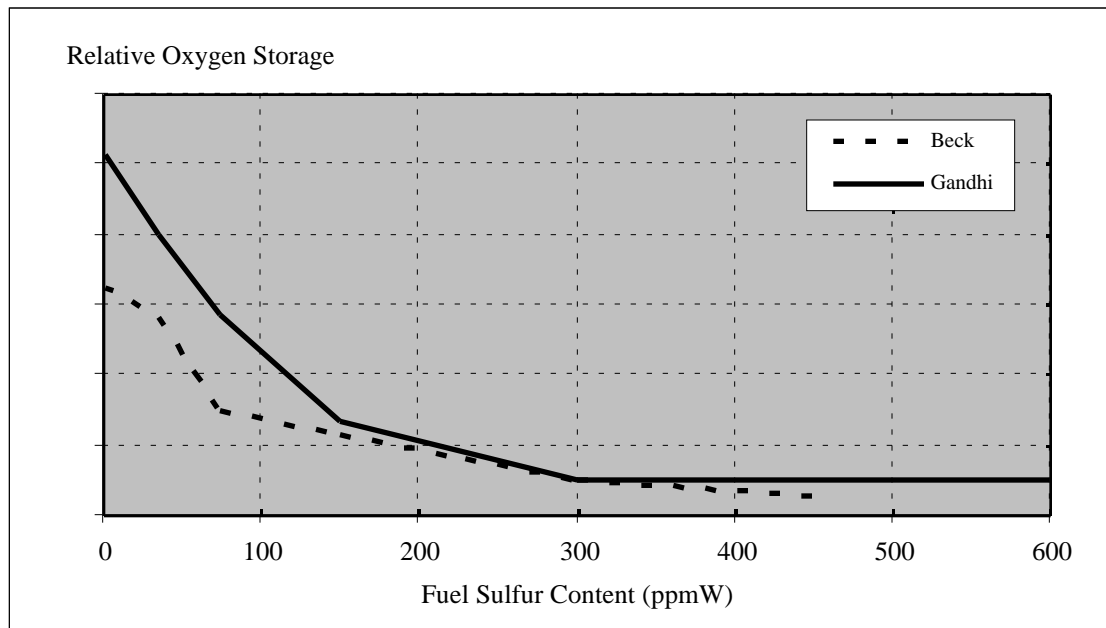


Figure 4-3. Effect of Sulfur on Oxygen Storage Capacity^{32,34}

Prior to the advent of EGO sensor-based OBD II catalyst monitoring, EGO sensor function was limited to providing the feedback necessary to dynamically adjust combustion air/fuel ratio. To facilitate the performance of this function, EGO sensors were generally located upstream of the catalytic converter (to allow evaluation of the engine-out oxidation state) in a high temperature operating environment (to achieve quick light-off of the required platinum catalysis). In these higher temperature environments, EGO sensors were somewhat less sensitive to precious metal sulfur poisoning since such poisoning has been shown to be inhibited above 650°C or so (precious metal surfaces are, in fact, “cleaned” of the effects of lower temperature sulfur poisoning when subjected to temperatures above 650°C). Although typical upstream EGO sensor operation occurs over a substantial range of temperatures (300-850°C), significant operation in the upper end of this range is not uncommon. Additionally, platinum has been shown to be somewhat less sensitive to sulfur than other precious metals such as palladium.

Nevertheless, several researchers, including Hepburn, Sweppy, and Zaghati,³⁵ have demonstrated small increases in EGO sensor response time and depressions in EGO sensor switching amplitudes with large increases (e.g., 0 to 1000 ppmW) in fuel sulfur.

The issue of greater concern relative to sulfur and EGO sensor interaction derives from the fact that auto manufacturers have recently incorporated the use of dual EGO sensors into vehicle designs to accomplish the catalyst monitoring functions of OBD II. In implementing this system, auto manufacturers are depending on a recognized relationship between declines in catalyst oxygen storage performance and declines in HC conversion efficiency and are actually monitoring the former to predict the latter. The ability of dual oxygen sensors to provide a dynamic determination of catalyst oxygen storage performance has been recognized for some time. In 1980, Meitzler demonstrated the basic mechanism using two EGO sensors, one located upstream and one located downstream of the converter.⁴³ By comparing the downstream EGO sensor output to that of the upstream sensor following known perturbations of the combustion air/fuel ratio between rich and lean states, Meitzler showed that the oxygen storage capacity of the catalytic converter could be estimated. On a shift from rich to lean, the downstream sensor maintains a rich output signal for some discrete period of time after the output from the upstream EGO sensor goes lean. This delay reflects the period during which the catalyst is storing the excess oxygen associated with the lean shift. Following a subsequent air/fuel ratio shift back to rich, the downstream EGO sensor again experiences an output switching delay as stored oxygen is released from the catalyst. Auto manufacturers have elected to meet the OBD II catalyst monitoring requirement using an equivalent dual EGO sensor algorithm which detects the ratio of output amplitudes at the downstream and upstream EGO sensors (a metric commonly referred to as the “oxygen storage index”).

Figure 4-4 presents data on the sensitivity of the dual EGO sensor-based oxygen storage index to variations in fuel sulfur. As was the case for catalyst oxygen storage impacts, as presented in

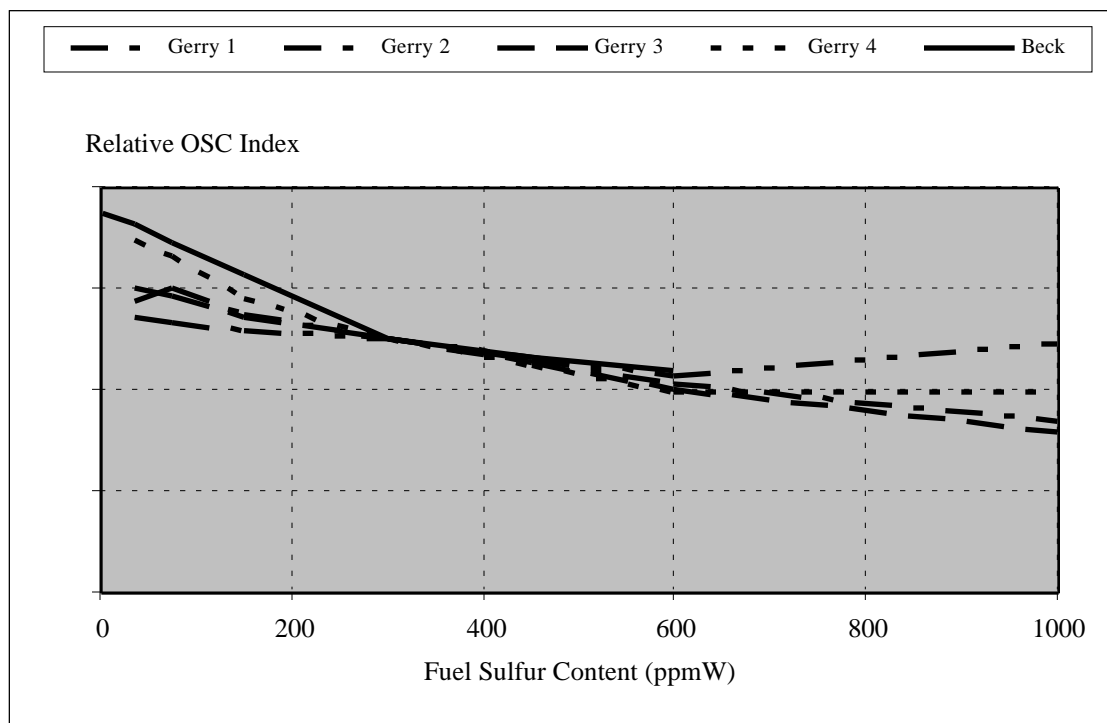


Figure 4-4. Effect of Sulfur on OSC Index^{33,34}

Figure 4-3, the oxygen storage indices have been normalized (with the index for 300 ppmW sulfur again serving as the unity value) to facilitate comparison across studies. The data presented in Figure 4-4 was derived from studies by Gerry and Beck.^{33,34} As was the case for the catalyst oxygen storage capacity presented in Figure 4-3, we note that the Gerry and Beck data are fairly consistent and again exhibit the greatest sensitivity at low sulfur levels, but also that these data reflect a substantially reduced sulfur sensitivity relative to the actual catalyst oxygen storage capacities determined by Gandhi and Beck.

The reduced sensitivity of the EGO sensor-based oxygen storage index (relative to the sensitivity of actual catalyst oxygen storage capacity) is due to two specific phenomena. First, some of the reduction in catalyst oxygen storage capacity is masked by the oxidation of sulfur deposited on catalyst precious metal surfaces during rich to lean transients. This oxygen consumption appears no different in terms of EGO sensor output than consumption associated with catalyst washcoat

oxygen storage. Second, sulfur has been shown to dampen both EGO sensor response time and output amplitude. Again, this effect mimics EGO sensor response during oxygen storage. Combined, these sulfur-driven effects serve to artificially inflate the apparent oxygen storage capacity of a sulfur poisoned system, reducing the effectiveness of the OBD II catalyst monitoring function (albeit generally in favor of errors of omission since oxygen storage is likely overstated at high fuel sulfur levels).

Figure 4-5, as extracted from work by Rabinowitz et al.⁴³, presents a good illustration of the sulfur-driven false pass potential of EGO-based catalyst performance monitors. From this figure, we note that an OBD II catalyst monitor for the system tested by Rabinowitz and calibrated on 100 ppmW sulfur fuel would equate oxygen storage delays of six and two seconds for HC conversion efficiencies of 92.5 (fresh catalyst) and 89 (aged catalyst) percent respectively. Furthermore, we see that although actual HC conversion efficiency has declined to 86 percent on a 350 ppmW sulfur fuel, the OBD II monitor predicts a conversion efficiency of over 90 percent due to a measured EGO sensor delay of three seconds.

4.3.3 NO_x Adsorber/Lean NO_x Catalyst Effects

Due to the potential for significant reductions in fuel consumption, lean-burn combustion is an active area of automotive research. Under such operation, both HC and CO emissions could be controlled to very low levels given excess air availability and the high efficiency of oxidation catalysis which could easily be integrated into such applications. Very lean combustion can also result in low engine-out NO_x emissions. Nevertheless, the ability of lean-burn vehicles to meet very low NO_x standards depends largely on the continued advancement of post-combustion NO_x controls such as lean NO_x catalysts and/or NO_x adsorbers (which collect NO_x under normal lean operation and are periodically purged using intentional short stoichiometric or slightly rich air/fuel ratio perturbation). While advancements in both systems have occurred, fundamental development work is ongoing.

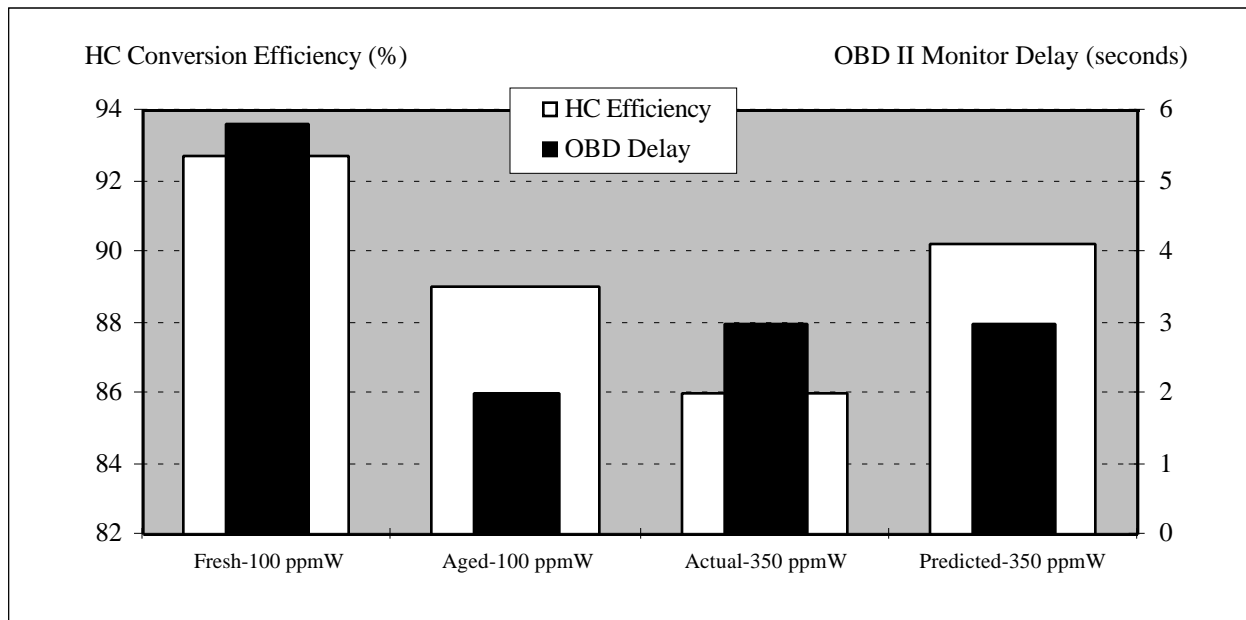


Figure 4-5. Illustrative Sulfur Effect on OBD II Monitor Performance⁴³

Since lean-burn NO_x control systems are not yet commercial for very low NO_x applications, it is not possible to draw on any in-use experience in evaluating the potential impacts of fuel sulfur on system performance. However, from discussions with catalyst manufacturers active in the area of NO_x adsorber research, we understand that such adsorbers are very sensitive to fuel sulfur levels and easily poisoned, much more so than current automotive catalysts. Furthermore, we understand that lean NO_x catalysts exhibit similar sulfur sensitivity. Figure 4-6 presents an illustration of potential lean NO_x catalyst sulfur sensitivity using data developed by Takei et al.³⁸ As indicated, the significant deactivation potential of even low sulfur fuels is obvious and the loss of conversion efficiency for even the 300 ppmW sulfur levels of common commercial fuels exceeds 50 percentage points. Apparent efficiency losses are significant even at the low sulfur levels of fuels such as CaRFG.

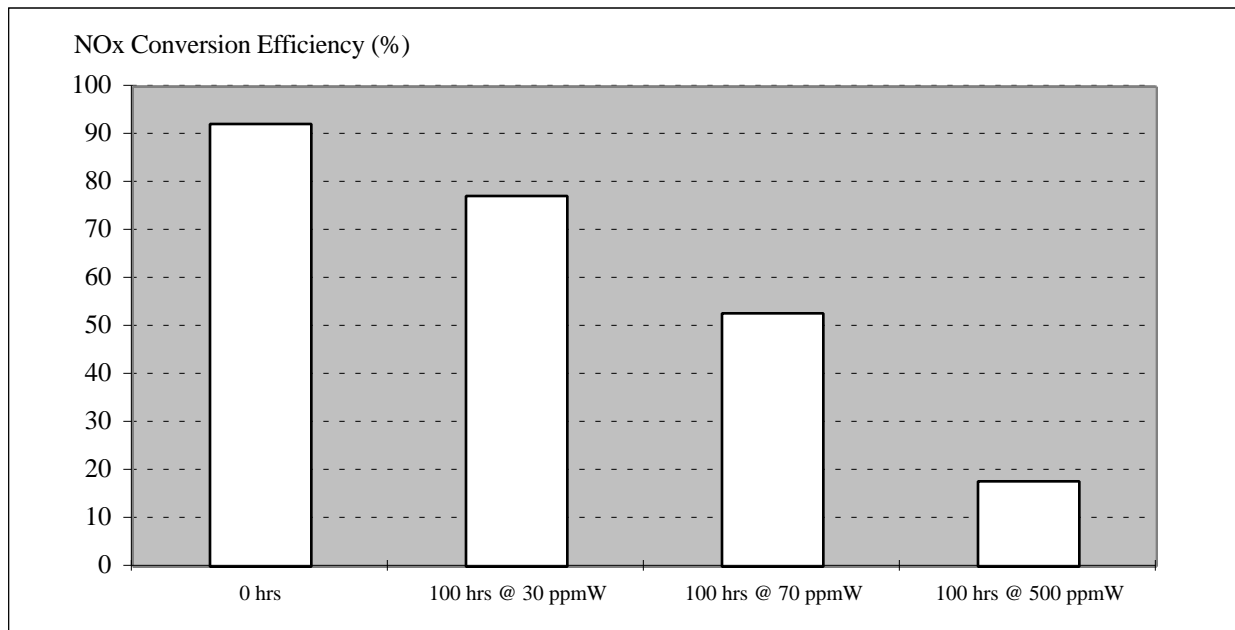


Figure 4-6. Sulfur Sensitivity of a Lean NO_x Catalyst³⁸

4.4 SULFUR TOLERANT SYSTEMS

In response to the recent focus on sulfur-driven catalyst and OBD impacts, all automotive catalyst manufacturers are conducting research into improving the sulfur tolerance of both precious metals and catalyst washcoats. Modifications to washcoat/precious metal formulations and washcoat/precious metal architecture have demonstrated limited improvements in catalyst activity and light-off performance under high sulfur operating conditions. However, no application has yet been developed which is not subject to significant deactivation with increasing fuel sulfur. In discussions with EEA, catalyst manufacturers have indicated that, in general, advances in catalyst activity and durability under low sulfur operating conditions usually also translate into improvements in high sulfur activity and durability.

Both Johnson Matthey^{41,45} and Degussa⁴⁰ have published data on catalyst formulations that are more tolerant of high fuel sulfur. Table 4-2 summarizes stabilized performance data for the improved Johnson Matthey formulation relative to an equivalent catalyst with a typical, currently available commercial formulation. Both catalysts are 0.90 liters in volume and loaded at 3.88 grams Pd per liter on a 400 cell per square inch/6 mil ceramic substrate. The current commercial catalyst includes a standard oxygen storage component (OSC) formulation with a Lanthanum promoter. Improvements to the new formulation include a more stable and active OSC composition and an improved Pd application method which enhances Pd/OSC interaction.

Catalyst Formulation	Fuel Sulfur (ppmW)	HC Efficiency (%)	CO Efficiency (%)	NO _x Efficiency (%)
Standard	0	98	86	87
	1000	97	78	76
	0	97	82	82
Improved	0	98	89	95
	1000	97	82	85
	0	97	87	93

Table 4-2. Sulfur Tolerance of Standard vs. Improved Catalyst Formulation⁴⁵

From Table 4-2, it is obvious that the improved Johnson Matthey formulation does exhibit improved high sulfur activity, but it is also obvious that this improvement is generally a result of higher low sulfur activity and that significant deactivation due to sulfur continues to be evidenced for both the standard and improved formulations. Perhaps the most important aspect of this improved formulation is its ability to recover its pre-poisoned activity after the removal of the high sulfur feedgas (without high temperature regeneration), whereas the standard formulation

exhibits substantial residual poisoning effects. Discussions with major catalyst manufacturers indicate that this data is reflective of the current state-of-the-art in terms of sulfur tolerance and that while additional developments may be possible (especially in terms of continuing improvements in overall catalyst activity), it is not possible to speculate on either the ultimate level of success or timing of future advancements.

During discussions with catalyst manufacturers, EEA was informed that catalysts with improved formulations equivalent to that presented by Johnson Matthey should be available for use on model year 1999 vehicles. None of the manufacturers was prepared to offer data on cost differentials for such improved formulations, but to the extent that improvements are achieved through better overall catalyst activity, these costs will be borne through a necessity to comply with more stringent emission standards (since there is currently no “penalty” for sulfur-driven deactivation by fuels with higher sulfur contents than those used during vehicle certification). It is EEA’s understanding that catalyst manufacturers will be issuing a “white paper” on sulfur-driven deactivation and sulfur tolerance within the next few weeks through their industry association, the Manufacturers of Emission Controls Association (MECA). EEA had hoped to reference this white paper in this report, but the paper was not completed in time for inclusion.

In addition to improvements in sulfur tolerance through advances in catalyst formulation, some level of additional tolerance can be gained by optimizing catalyst location and engine calibration in response to known features of sulfur-driven deactivation. First, precious metal poisoning has been shown to be inhibited under high temperatures (greater than 650°C), although it should be noted that poisoning of the catalyst oxygen storage component has been demonstrated to occur even at considerably higher temperatures. The thermal durability of today’s formulations generally allows catalysts to be mounted far forward in the exhaust stream, in many cases as far forward as the exhaust manifold. Although EEA was unable to locate any specific data on sulfur tolerance as a function of catalyst mounting location, the sensitivity of catalyst poisoning to temperature is generally accepted (see, for example, Gandhi³²) and is most severe under moderate

catalyst temperatures (400-600°C). Therefore, extreme close-coupling may be a viable method of improving sulfur tolerance on vehicles with adequate underhood space. Second, there is some evidence that catalysts are more tolerant of sulfur under specific engine calibrations (such as lean spike strategies^{41,42}), although no rigorous studies of LEV or ULEV level systems have been conducted to quantify potential improvements.

Increasing catalyst size and/or precious metal loading may also lead to some improvement in catalyst sulfur tolerance by increasing overall catalysis capacity, but this increase would have to be costed solely as a function of improving sulfur tolerance since emissions compliance on a low sulfur fuel could always be demonstrated with smaller or lower loading catalysts. EEA has previously estimated the costs of increased catalyst size and loading for EPA as part of the Agency's review of the supplemental FTP test procedure requirements.⁴⁶ Increasing the quantity of sulfur scavengers (such as nickel) in catalyst formulations could also produce advances in catalyst sulfur sensitivity, although such advances generally come at the expense of overall catalyst activity and, therefore, are not currently considered as practical solutions.

Despite advances in the understanding of fuel sulfur impacts and efforts by catalyst manufacturers to design systems more tolerant of fuel sulfur, it is not apparent that the auto industry has undertaken a dedicated effort to evaluate technology responses with the potential to alleviate the emissions impacts of high sulfur fuels. For example, EEA was unable to find any research papers investigating the potential of addressing fuel sulfur through engine-based technology advancements. Can fuel sulfur sensing and feedback systems be used to tailor engine operation or emissions control system performance in accordance with in-use fuel properties? Or can active systems be designed which respond to sulfur-driven catalyst deactivation by periodically creating the necessary high temperature conditions required to reverse or minimize sulfur poisoning effects (similar to particulate trap regeneration systems)? Research in such areas is conspicuously lacking from the considerable sulfur studies undertaken over the last several

years and without such research it will be very difficult to gain a proper perspective on alternatives to, or the cost effectiveness of, automotive fuel desulfurization.

Similarly, EEA is not aware of any specific efforts to improve the sulfur tolerance of EGO sensors. Generally, however, the sulfur related impacts on EGO sensor-based OBD II catalyst monitor performance are more a function of the consumption of oxygen by surface-bound sulfur in the catalyst rather than EGO sensor deactivation per se. Nevertheless, research has shown delayed response due to direct EGO sensor poisoning.³⁵ The sulfur sensitivity of both lean NO_x catalysts and NO_x adsorbers is being addressed as an integral component of development research for both systems. Since neither is currently considered to be commercial technology for very low NO_x applications, it is not possible to speculate on what, if any, additional costs will be associated with specifically addressing sulfur sensitivity.

4.5 REFERENCES

1. Weaver, E.E., Shiller, J.W., Campau, R.M., Macura, J.F., "Ford 450 Car Catalyst Field Test", SAE Technical Paper 741061, 1974.
2. Summers, J.C., Baron, K., "The Effects of SO₂ on the Performance of Noble Metal Catalysts in Automobile Exhaust", General Motors Research Publication GMR-2729, June 1978.
3. Cheng, C.C., "Effect of Sulfur Dioxide on the Oxidation of Carbon Monoxide Over Platinum-Alumina", General Motors Research Publication GMR-2781, August 1978.
4. Weaver, E.E., "Sulfur Levels in California Non-Leaded Fuels", Ford Motor Company Interoffice Memorandum to Mr. D.A. Jensen, October 23, 1978.
5. Williamson, W.B., Gandhi, H.S., Heyde, M.E., Zawacki, G.A., "Deactivation of Three-Way Catalysts by Fuel Contaminants: - Lead, Phosphorus and Sulfur, SAE Technical Paper 790942, 1979.

6. Joy, G.C., Lester, G.R., Molinaro, F.S., "The Influence of Sulfur Species on the Laboratory Performance of Automotive Three Component Control Catalysts", SAE Technical Paper 790943, 1979.
7. Williamson, W.B., Stepien, H.K., Gandhi, H.S., "Poisoning of Platinum-Rhodium Automotive Three-Way Catalysts: Behavior of Single-Component Catalysts and Effects of Sulfur and Phosphorus, *Environ. Sci. Technol.*, 14:319-324, March, 1980.
8. "Regulation of Fuels and Fuel Additives: Fuel Quality Regulations for Highway Diesel Fuel Sold in 1993 and Later Calendar Years", U.S. Environmental Protection Agency, *Federal Register*, 55:34120-34151, August 21, 1990.
9. "Standard Specification for Automotive Spark-Ignition Engine Fuel", American Society for Testing and Materials, Standard D4814.
10. "Standard Specification for Automotive Gasoline", American Society for Testing and Materials, Standard D439.
11. "Regulation of Fuels and Fuel Additives: Standards for Reformulated and Conventional Gasoline", U.S. Environmental Protection Agency, *Federal Register*, 59:7716-7878, February 16, 1994.
12. "Compliance Assistance Program, Gasoline Marketing and Distribution, Fuel Specifications", California Air Resources Board, July 1989.
13. "California Phase 2 Reformulated Gasoline Specifications, Technical Support Document", California Air Resources Board, October 4, 1991.
14. "Standard Specification for Diesel Fuel Oils", American Society for Testing and Materials, Standard D975.
15. Searles, R.A., "State of the Art and Future Potential Catalytic Emission Control Systems for meeting European 2000/2005 Emission Standards", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
16. Takei, Y., Shipinski, J., Crary, B., "Toyota's Experience and Perspective on Sulfur in Gasoline", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.

17. Furey, R.L., Monroe, D.R., "Fuel Sulfur Effects on the Performance of Automotive Three-Way Catalysts during Vehicle Emissions Tests", SAE Technical Paper 811228, 1981.
18. "Effects of Fuel Sulfur Levels on Mass Exhaust Emissions", Technical Bulletin No. 2, Auto/Oil Air Quality Improvement Research Program, February, 1991.
19. "Effects of Fuel Sulfur on Mass Exhaust Emissions, Air Toxics, and Reactivity", Technical Bulletin No. 8, Auto/Oil Air Quality Improvement Research Program, February, 1992.
20. Hammerle, R.H., Truex, T.J., "The Kinetics of SO₂ Oxidation for Various Catalyst Compositions", SAE Technical paper 760090, 1976.
21. Laresgoiti, A., Springer, G.S., "Sulfate and Particulate Emissions from an Oxidation Catalyst Equipped Engine", *Environ. Sci. Technol.*, 11:285-292, March, 1977.
22. Somers, J.H., Garbe, R.J., Lawrence, R.D., Baines, T.M., "Automotive Sulfate Emissions - A Baseline Study", SAE Technical Paper 770166, 1977.
23. McKee, D.E., "Effects of Engine Parameters and Catalyst Composition on Vehicle Sulfate Emissions", SAE Technical Paper 770167, 1977.
24. Mikkor, M., Hammerle, R.H., Truex, T.J., "Effects of Hydrocarbons, Carbon Monoxide, and Oxygen of Sulfuric Acid Emission from an Automotive Catalyst", *Ind. Eng. Chem., Prod. Res. Dev.*, 16: 217-222, September 1977.
25. Summers, J.C., "The Reaction of Sulfur Oxides with Alumina and Pt/Alumina", General Motors Research Publication GMR-2718, May 1978.
26. Ingalls, M.N., Springer, K.J., Lawrence, R.D., "Automotive Sulfates - A CVS Compatible Sampling System", SAE Technical Paper 780644, 1978.
27. Ingalls, M.N., Bruetsch, R.I., "Evaluation of a Low Sulfate Emission Control System", SAE Technical Paper 800821, 1980.
28. "Program Final Report", Auto/Oil Air Quality Improvement Research Program, January 1997.
29. Summers, J.C., Skowron, W.B., Williamson, W.B., Mitchell, K.I., "Fuel Sulfur Effects on Automotive Catalyst Performance", SAE Technical Paper 920558, 1992.

30. Beck, D.D., Sommers, J.W., DiMaggio, C.L., "Impact of Sulfur on Model Palladium-Only Catalysts Under Simulated Three-Way Operation", *Appl. Catal. B* 3, 205-227, 1994.
31. Thoss, J.E., Rieck, J.S., Bennett, C.J., "The Impact of Fuel Sulfur Level on FTP Emissions - Effect of PGM Catalyst Type", SAE Technical Paper 970737, 1997.
32. Gandhi, H.S., "Effect of Fuel Sulfur on Automotive Three Way Catalysts", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
33. Gerry, F., "Results from the CRC Laboratory Study of Sulfur Effects on Catalysts and OBD II Systems", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
34. Beck, D.D., "The Impact of Sulfur on On-Board Diagnostic Systems", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
35. Hepburn, J., Sweppy, M.S., Zaghati, Z.N., "The Effect of Fuel Sulfur on Ford's OBD-II Catalyst Monitor", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
36. Paggi, R., "Is It Really a Technology Hurdle? New Test Data and Programs Conducted by the Oil Industry", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
37. Jetter, J., "Honda's LEV and ULEV Technology for 1998 and the Impact of Fuel Properties", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
38. Takei, Y., Shipinski, J., Crary, B., "Toyota's Experience and Perspective on Sulfur in Gasoline", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
39. Rech, H., Schafer, Dr. H.-V., "Effect of Gasoline Sulfur on TLEV Vehicle Emission Control Performance", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.

40. Garr, G.T., "Effects of SO₂ on Catalyst Performance", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
41. Bennett, C., Cooper, B.J., "The Relative Effects of Catalyst Design and Vehicle Calibration On Vehicle Emissions in the Presence of Elevated Fuel Sulfur Levels", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
42. Robota, H., Williamson, W.B., "Impact of Fuel Sulfur in Meeting Advanced Emission Standards", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
43. Rabinowitz, H., Tauster, S., Amundsen, A., "Recent Insight on the Effect of Sulfur on Modern Three Way Catalysts", presented at the CRC Auto/Oil Symposium: The Search for Sulfur-Tolerant Emission Control Systems, Dearborn, Michigan, September 11-12, 1997.
44. Meitzler, A.H., "Application of Exhaust-Gas-Oxygen Sensors to the Study of Storage Effects in Automotive Three-Way Catalysts", SAE Technical Paper 800019, 1980.
45. Andersen, P.J. Rieck, J.S., "Advances in Pd Containing Three Way Catalyst Activity", SAE Technical Paper 970739, 1997.
46. Energy and Environmental Analysis, Inc., "Assessment of Technology Costs to Comply with Proposed FTP Revisions", prepared for the U.S. Environmental Protection Agency, September 1995.

ADDENDUM

A REVIEW OF PRIMARY AND SECONDARY PARTICULATE MATTER ASSOCIATED WITH LIGHT-DUTY VEHICLES

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1. OVERVIEW.

Under subcontract with Sierra Research, Inc., Energy and Environmental Analysis, Inc. (EEA) was retained by the U.S. Environmental Protection Agency (EPA) to perform a literature review of light-duty motor vehicle particulate matter (PM) emissions. This review entailed the investigation of both primary and secondary particulate and included the assessment of PM emission (or formation) rates and light-duty vehicle-related PM size distributions. This paper summarizes the results of EEA's review.

Atmospheric particulate has been regulated for a number of years due to human health concerns, visibility impacts, the ability of airborne particulate to degrade materials (such as rubber), and particulate-related soiling. National Ambient Air Quality Standards (NAAQS) were initially expressed in terms of total suspended particulate (TSP). However, in recognition of the relationship between human respiration and particle size, the particulate NAAQS were restructured to apply only to those particles with "an aerodynamic diameter less than or equal to a nominal 10 micrometers (μm).\" This particle fraction is commonly known as PM₁₀. In recent years, concerns over the human health implications of airborne particulate have escalated and the EPA has recently adopted a supplemental ambient air quality standard for particulate with an aerodynamic diameter of 2.5 μm or less (PM-2.5). These ambient standards are not a focus of this literature review, but they do provide the basic context for the review as well as one measure against which light-duty vehicle particulate production rates can be assessed.

In conducting this review, EEA attempted to assemble the latest available material on each topic addressed. However, given the wide range of publications in which atmospheric-related particulate studies appear, including national and international publications focusing on meteorological, chemical, environmental, and motor vehicle-related topics, it is not possible to assemble a complete package of particulate-related publications in a limited timespan. Moreover, since much particulate research, especially that for secondary particulate, is theoretical in nature, overall research has been continually evolving over at least the last three decades and the total

number of research papers available in the various publications is overwhelming. By focusing on the latest papers augmented with key historical papers, a comprehensive set of research papers covering the full range of requested topics has been assembled and reviewed. Should a more detailed study of any topic be desired, each reference paper used for this review provides more comprehensive set of references on which to base further research.

2. PRIMARY PARTICULATE EMISSIONS FROM LIGHT-DUTY VEHICLES.

As per EPA directive, current technology light-duty gasoline vehicles are the major focus of the literature search on primary particulate emissions. This focus places a significant constraint on the resources available for review since Tier I particulate emission standards have only been applicable since the 1994 model year for light-duty vehicles and the 1995 model year for light-duty trucks. Moreover, these standards were phased-in over three model years, so there is no guarantee that vehicles during the first few Tier I model years are, in fact, Tier I vehicles (unless so-stated in the material reviewed). Prior to the advent of Tier I and relatively recent concerns over fine particulate, most light-duty particulate emission rate studies were targeted at diesel vehicles as a result of their inherently higher emission rates relative to equivalent gasoline vehicles. Nevertheless, given the continued particulate nonattainment status of many areas of the U.S. and the recently adopted PM-2.5 ambient particulate standard, there is a renewed interest in gasoline vehicle particulate emissions.

There are two major studies of light-duty gasoline vehicle particulate emissions currently underway. Unfortunately, neither study is complete and, therefore, the literature available for review consists primarily of project descriptions. EEA was, however, able to locate interim unpublished reports for each study and the information derived from these reports is discussed below. As both studies are ongoing and there will undoubtedly be a wealth of additional data released over the next several months, EPA should monitor their status on a continuing basis to augment the data presented here. Given the "raw" nature of the data presented for these two studies, some analysis effort has been expended to ensure its proper characterization. Additional review materials are summarized more succinctly in light of their developed nature.

2.1 The Environmental Research Consortium's "Current Vehicle Particulate Emissions Characterization" Project

The Environmental Research Consortium (ERC) is a working group of the United States Council for Automotive Research (USCAR). USCAR was formed in 1992 by Chrysler, Ford, and General Motors to monitor and conduct automotive-related research. As part of an on-going project, the ERC is collecting primary exhaust particulate emissions data for late model light-duty gasoline vehicles. Project vehicles consist of several high sales volume light-duty car and truck models of each consortium member. Both low and high mileage vehicles are to be tested over the Federal Test Procedure (FTP) and particulate emissions will be investigated separately for each of the three phases of the FTP. To ensure adequate sample mass, each particulate "test" consists of four consecutive cold start FTP's. The primary test fuel for the project is a Howell California Phase II Reformulated Gasoline (RFG), although some testing has also been performed using Howell EEE (indolene).

EEA located a synopsis of project test data in the dockets for the recent ozone and particulate matter National Ambient Air Quality Standard (NAAQS) revisions (Docket Nos. A-95-54, A-95-58, A-95-38, and A-96-51)¹. This project test data was included as Attachment 30 to March 12, 1997 comments submitted by the American Automobile Manufacturers Association (AAMA). EEA contacted the manager for the ERC project to investigate whether a more complete study report was available, but was informed that no additional data had been released. Therefore, our review of ERC project data is limited to that presented in the ozone and particulate matter dockets. Due to the uncopyrighted nature of the docket submission, a copy of the complete docket materials is included as Attachment 1.

Figure 1 is a summary of the ERC particulate data. In developing Figure 1, the separate test results for the two light-duty vehicles and five light-duty trucks subjected to replicate testing (as listed in Attachment 1) were arithmetically averaged to avoid overweighting the emission rates from these vehicles. As illustrated, the particulate emission rates for all 19 vehicles tested were

over an order of magnitude less than the applicable 80 and 100 milligram per mile (mg/mi) emission standards for light-duty Tier I vehicles and trucks. In fact, the light-duty vehicle emission rates are a full two orders of magnitude below applicable standards. The measured emission rates for light-duty vehicles are generally below 1 mg/mi, with the emission rates for light-duty trucks ranging from 0.5 to 2 mg/mi. The average light-duty truck emission rate of 1.34 mg/mi is exactly twice the light-duty vehicle average of 0.67 mg/mi.*

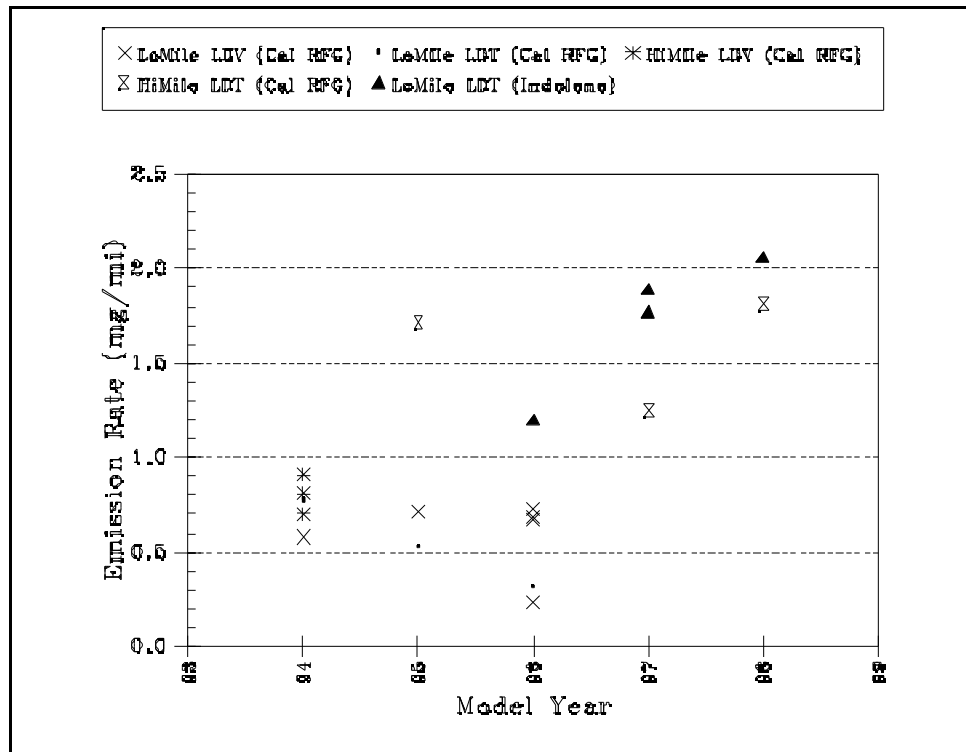


Figure 1. ERC Particulate Emission Rates

* The indicated means treat light-duty truck indolene and California RFG emissions testing in the aggregate. If only California RFG tests are considered, the average light-duty truck emission rate declines to 0.54 mg/mi and emission rates for light-duty trucks and light-duty vehicles are indistinguishable.

Relative to the light-duty trucks tested on California RFG, those tested on indolene appear to emit, on average, about 3 times more particulate over the composite FTP (no light-duty vehicle indolene data is presented in the material available for review). For individual phases of the FTP, the average ratio between trucks tested with indolene and trucks tested with California RFG is 3.5 for Phase 1, 2.4 for Phase 2, and 4.0 for Phase 3. Given the low aromatic, low sulfur properties of indolene, differences of this magnitude seem large, but since specific fuel specifications are not provided in the docket data it is not possible to speculate on potential causes. However, a similar comparison of indolene emission rates to California RFG emission rates for hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) indicates that indolene emission rates are lower on average for all three pollutants. Based on this counter intuitive relationship for HC, CO, and NO_x, it appears that there may be greater variability across test vehicles than across test fuels and, therefore, it is probably not possible to draw any fuel-specific conclusions from the dataset reviewed.

The ERC dataset includes both low and high mileage vehicles, although the number of high mileage vehicles is limited (three light-duty vehicles and three light-duty trucks). The mean emission rate for both high mileage light-duty vehicles (0.81 mg/mi) and light-duty trucks (1.60 mg/mi) exceeds that of low mileage light-duty vehicles (0.60 mg/mi) and low mileage light-duty trucks (1.22 mg/mi). However, it is not possible to draw any distinct conclusions from this dataset regarding particulate emissions deterioration since the standard deviations of emission rates measurements are of sufficient magnitude to independently differentiate low and high mileage vehicles. As was the case for fuel differentials, it appears that vehicle-to-vehicle variability is a more important factor in this dataset than mileage variability. A statistically significant difference between low and high mileage trucks is observed if the indolene tests are excluded from the low mileage sample (the low mileage mean drops to 0.54 mg/mi). However, given the fuel-related issues noted above, this difference should still be viewed with some caution. Interestingly, while no statistically significant difference can be noted between low mileage light-duty vehicles and trucks in the ERC dataset (regardless of truck fuel), high mileage truck

particulate emission rates exceed high mileage light-duty vehicle emission rates by a statistically significant margin.

ERC particulate measurements for component FTP phases indicate that on average Phase 1 (cold start) emission rates exceed composite FTP rates by about a factor of two for both light-duty vehicles and light-duty trucks. Stabilized (FTP Phase 2) emission rates are 50-70 percent of composite rates, while hot-start (FTP Phase 3) emission rates are approximately equal to overall composite rates.

The ERC test program is designed to include replicate testing on about 50 percent of project vehicles and replicate test results for seven vehicles are included in the dataset presented in Attachment 1. This replicate data is perhaps one of the key elements to come out of the ERC program since even a very brief review of the data indicates potential problem areas. While HC, CO, and NO_x emission rates across replicate tests vary from 0-17 percent (with average absolute deviations of 9 percent for HC, 7 percent for CO, and 5 percent for NO_x), measured PM emission rates across tests vary by 9-64 percent (with an average absolute deviation of 34 percent).^{*} Over component FTP phases, the observed variation in PM emissions is even larger. Over Phase 1, absolute variation averages 35 percent, but ranges up to 100 percent. Phase 2 absolute average variation is 69 percent, ranging as high as 284 percent. Phase 3 absolute variation ranges as high as 100 percent and averages 48 percent. The significance of these variations is magnified when one considers that each "individual" test consists of four complete FTP cycles, thereby allowing for substantial pre-measurement "averaging" to occur before individual test results are reported. Clearly, test-to-test variability is an issue of concern with the ERC dataset (and perhaps with motor vehicle particulate measurement in general).

^{*} As used in the context of replicate testing analysis in this paper, the terms "variation", "maximum variation", and "average absolute variation" are defined as follows. Variation is the relative change between measurement 2 and measurement 1 (i.e., measurement 2 divided by measurement 1 minus one). Maximum variation is the largest absolute difference between calculated variability and unity. Average absolute variation is the arithmetic average of the absolute differences between calculated variability and unity (absolute differences are used to overcome the masking influences of positive and negative variations).

2.2 The Coordinating Research Council's "Primary Particulate Emissions from Light-Duty Motor Vehicles" Project (CRC Project No. E-24)

The Coordinating Research Council (CRC) is currently conducting an extensive testing program designed to collect primary particulate emissions data from in-use light-duty gasoline and diesel vehicles. This program is being carried out under three separate studies. As part of the Northern Front Range Air Quality Study (NFRAQS), particulate mass emission rates will be collected in Colorado for 120 in-use vehicles during the summer and 70 in-use vehicles during the winter. In addition to mass measurements, the NFRAQS study will include both particulate composition and size distribution analysis. Under a second program study, the College of Engineering, Center for Environmental Research and Technology (CE-CERT) of the University of California, Riverside will collect emission rate data on 100 in-use vehicles. The CE-CERT study will also include analysis of particulate composition and size distribution. The third program study is being conducted by Southwest Research Institute (SwRI) and consists of particulate measurement on 60 light-duty vehicles. Like the other two study components, the SwRI study will also include particle size distribution analysis. Given vehicle test program size, this CRC project will be invaluable in analyzing the magnitude and character of light-duty vehicle particulate emissions. In all, emissions from over 350 light-duty vehicles will be measured and a significant fraction of particulate samples will be subjected to size distribution and composition analysis.

Unfortunately, the CRC project is not yet complete. It is EEA's understanding that most vehicle testing is complete, but that data reduction and analysis is ongoing. In accordance with funding requirements, no official program data have been publicly released to date. However, EEA was able to obtain a progress report for the NFRAQS portion of the CRC project that includes a presentation of particulate test results for 38 light-duty vehicles tested during the summer (4 diesels and 34 gasoline vehicles) as well as a synopsis of replicate FTP and IM240 test results for 6 vehicles tested during the summer and 24 vehicles tested during the winter². Since this progress report is not copyrighted, it is included as Attachment 2. Since there is very little

descriptive material on study protocols, etc. included in the progress report, the presented data must be considered preliminary. Nevertheless, this NFRAQS dataset represents the most extensive collection of current in-use vehicle particulate emission rates uncovered by EEA.

Figure 2 presents a summary of the NFRAQS summertime particulate data. Unfortunately, the wintertime data presented in the NFRAQS progress report does not include vehicle model year or fuel type and, as a result, can only be evaluated in an aggregate fashion until a more complete study report is available. Similarly, the NFRAQS dataset does not distinguish between light-duty vehicles and light-duty trucks and, therefore, all vehicles are treated in the aggregate. For comparative purposes, Figure 2 also includes the ERC dataset described above, as well as several other data points obtained from other sources to be described below.

A declining trend in light-duty gasoline vehicle particulate emission rates is readily observed. Figure 3 isolates the data points for these vehicles and presents the slope of the long-term trend developed through least squares regression analysis. The trend is exponential, as indicated by the y-axis in both Figures 2 and 3, and the indicated coefficient of 1.189 is significant at the 99 percent confidence level. It is not possible given the information in the NFRAQS progress report to disaggregate trend influences into age-based deterioration and vehicle technology components. However, since the observed trend holds for over a twenty year period during most of which no gasoline vehicle particulate standards were in effect and during half of which HC standards were constant, age-based deterioration is likely to play an important role in the observed trend. Nevertheless, technology advances during this same period have been significant and the phase-in of advanced technology over time would tend to dampen any step changes in emission rates. Therefore, a significant technology role cannot be definitively ruled out.

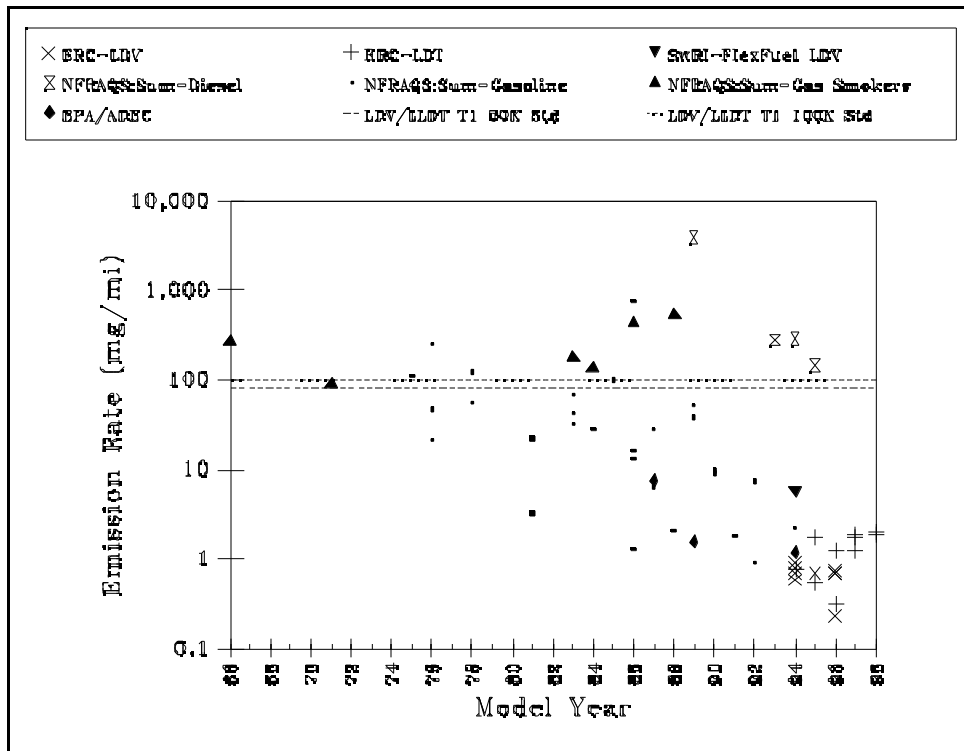


Figure 2. Particulate Emission Rates by Model Year

As indicated in Figure 2, the ERC dataset is reasonably consistent with the NFRAQS-implied trend although the sole 1994 and later NFRAQS data point has an emission rate over twice that of the highest emitting ERC vehicle of the same model year. In absolute terms, the difference is small at a little over 1 mg/mi, a level that is only 1 percent of the full life emission standard for light-duty vehicles. Mileage is a very unlikely contributor to this differential since three of the four ERC vehicles of that model year (1994) had accumulated over 89,000 miles. Some of the difference may result from the in-use nature of the NFRAQS test vehicles, but since the ERC dataset does not describe vehicle recruitment practices, it is not possible to elaborate further at this time.

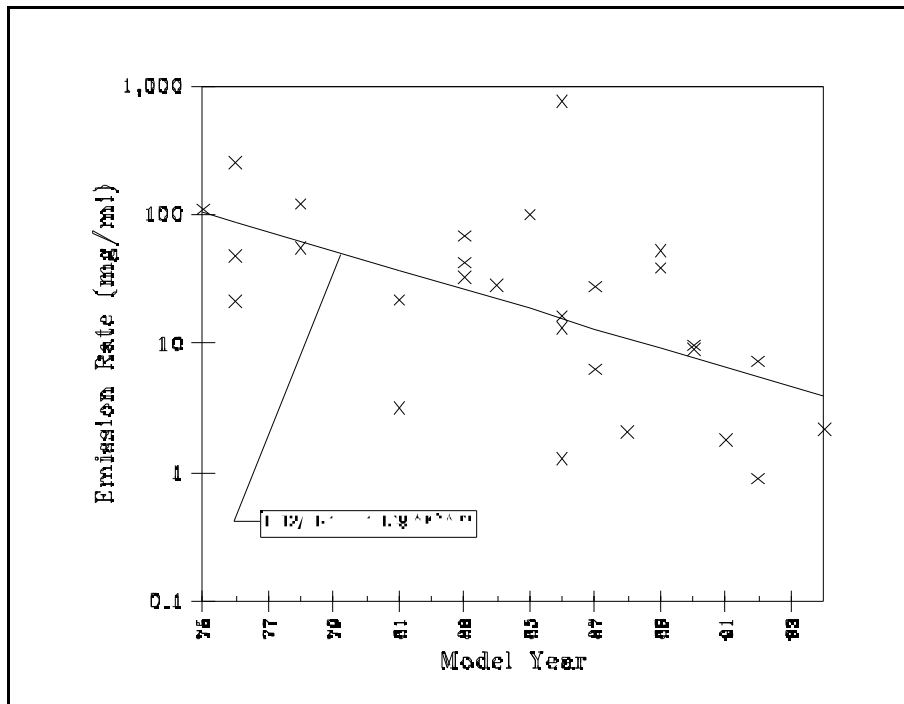


Figure 3. NFRAQS Summertime Particulate Emission Rates for Gasoline Vehicles

As indicated by the horizontal lines in Figure 2, not a single NFRAQS gasoline vehicle less than 10 years old exceeded the particulate emission standard for light-duty vehicles, even though these standards only became applicable with the 1994 model year. The effect of oil consumption on gasoline vehicle emission rates can be readily observed by the differentials between the NFRAQS-identified high smoke emitters and their non-smoking counterparts. For early-to-mid 1980's vehicles, this differential tended to be a factor of 3 or 4, but for the mid-to-late 1980's vehicles, the differential is more nearly an order of magnitude.

The NFRAQS dataset clearly shows the differential between light-duty gasoline and light-duty diesel emission rates. While only four diesel vehicles were tested, they were all of 1989 and later vintage and none meet either the 50,000 or 100,000 mile Tier I light-duty particulate standards met by all similarly aged gasoline vehicles. These Tier I cutoffs are intended to illustrate emission

differentials only. Certainly the pre-1994 NFRAQS diesel vehicles were not subject to the Tier I standards and it is also not clear that either the 1994 or 1995 diesel vehicles were certified to these standards (since only a portion of each model year's fleet was required to meet the standard prior to the 1996 or 1997 model year). On average, even ignoring the 1989 diesel vehicle which had an emission rate that was an order of magnitude higher than any other vehicle in the NFRAQS study, diesels still emit at a rate nearly two orders of magnitude higher than gasoline vehicles of post-1990 technology. Two of the three post-1990 diesel emit at rates exceeding the 1987-1993 model year particulate standard of 0.20 g/mi, but since these vehicles could have been certified through particulate averaging, their specific certification emissions limits are not certain.

Figure 4 is an enhancement of Figure 2 showing only 1990 and newer model year light-duty gasoline vehicles. As indicated, 100 percent of the 27 vehicles tested emitted particulate at rates below 10 mg/mi. 85 percent of the vehicles exhibit emission rates of 2 mg/mi or less. One interesting aspect of Figure 4, is that there is no obvious altitude effect evident when one compares the NFRAQS and ERC data. As indicated above, the ERC data generally follows the emission rate trend observed for NFRAQS vehicles over time and several of the post-1990 NFRAQS emission rates are of magnitudes similar to those of the ERC test vehicles.

In terms of seasonal (i.e., temperature) influences on emission rates, it is difficult to draw any definitive conclusions from the NFRAQS data because of the lack of wintertime vehicle age data. The overall average winter PM emission rate (98 mg/mi) exceeds the overall average summer rate (44 mg/mi) by over a factor of two. However, the corresponding ratio for CO (which we would expect to be similar) is less than 0.5 (16.8 g/mi winter vs. 38.7 g/mi summer) implying that there may be substantial differences (unrelated to season) in the summer and winter test populations. These same relationships generally hold true regardless of whether the NFRAQS IM240 data is included in the determination of the winter-to-summer ratio, thereby eliminating test cycle as a significant contributor to the observed differentials.

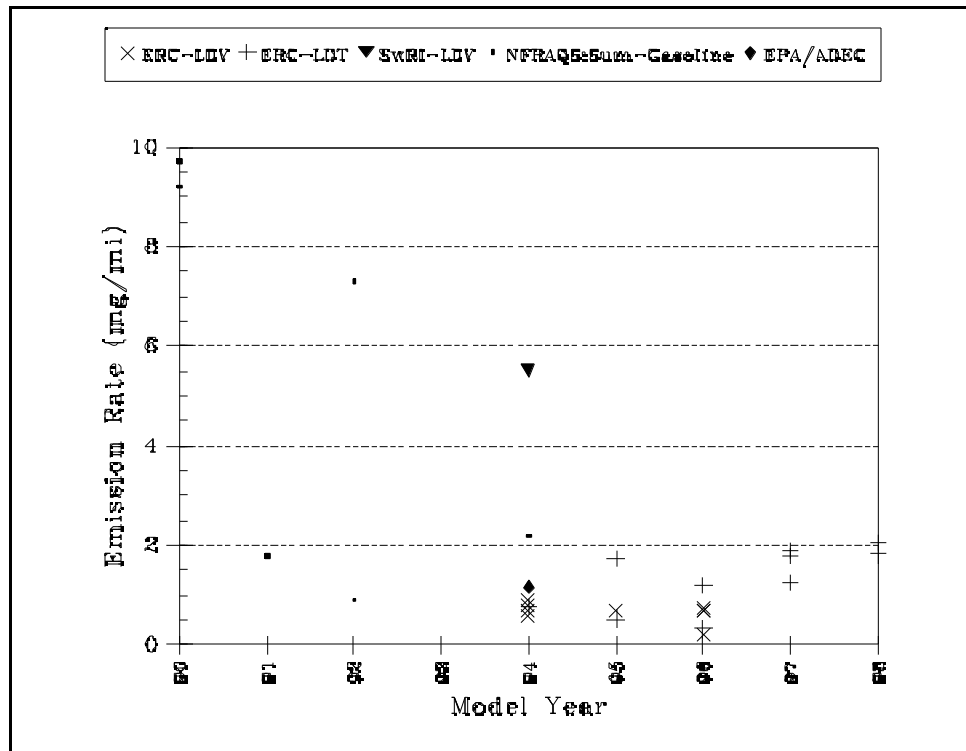


Figure 4. 1990 and Newer Model Year Particulate Emission Rates

Like the ERC data, the NFRAQS study includes replicate testing of a subset of study vehicles. Table 1 presents summary statistics for replicate testing results included in the NFRAQS progress report. Similar to the trends reported above for the ERC study, there is substantial variation between replicate NFRAQS particulate tests. Absolute replicate particulate emission rate variations average 35-55 percent regardless of the test subpopulation analyzed. IM240 data tends to exhibit the greatest variability, but even when this data is omitted from analysis, absolute variations in particulate emissions of up to 177 percent are observed. Similar data for HC, CO, and NO_x over the FTP indicate substantially less variability, with absolute average variations of about 10 percent and maximum variations of 10-50 percent.

Dataset	Statistic	PM	HC	CO	NO _x
NFRAQS (All Data)	Maximum Variation (%)	251	200	129	92
	Average Absolute Variation (%)	47	24	24	11
NFRAQS (All Summer Data)	Maximum Variation (%)	100	16	48	29
	Average Absolute Variation (%)	35	8	15	10
NFRAQS (All Winter Data)	Maximum Variation (%)	251	200	129	92
	Average Absolute Variation (%)	50	29	26	11
NFRAQS (Winter FTP Data)	Maximum Variation (%)	177	23	31	13
	Average Absolute Variation (%)	55	13	10	5
NFRAQS (Winter IM240 Data)	Maximum Variation (%)	251	200	129	92
	Average Absolute Variation (%)	47	38	35	15
NFRAQS (All EPA FTP Data)	Maximum Variation (%)	177	19	48	29
	Average Absolute Variation (%)	50	8	12	9
NFRAQS (All CDPHE FTP Data)	Maximum Variation (%)	125	23	31	13
	Average Absolute Variation (%)	42	13	12	6
ERC (All Data)	Maximum Variation (%)	64	17	17	13
	Average Absolute Variation (%)	34	9	7	5

Table 1. Variability Statistics for Replicate Particulate Tests

2.3 Published Materials

As stated above, the fact that Tier I technology has only recently been introduced limits the volume of published material available for review. EEA did, however, locate two recently published papers on particulate studies that included testing of 1994 light-duty vehicles. Fanick,

et al. (1996)³ at SwRI report particulate test results for one 1994 Ford Taurus flexible-fuel vehicle (FFV) certified to California Transitional Low Emissions Vehicle (TLEV) standards. Particulate emission rates were reported for the vehicle while operated on Federal Reformulated Gasoline (RFG), M85, E85, LPG, and CNG. Testing on the latter two fuels was accomplished through the installation of carbureted conversion kits and probably does not reflect the performance capabilities of advanced gaseous fuels equipment relying on finely-controlled fuel injection technology.

During most SwRI testing, the FFV was operated in a fuel rich condition to simulate a high particulate failure mode. However, baseline stoichiometric testing was also performed during operation on Federal RFG. This baseline data point is shown in both Figures 2 and 4; labeled as "SwRI-LDV". As indicated in the figures, the particulate emission rate of 5.5 mg/mi for the FFV at stoichiometry is from 2.5 to 8 times as large as the other data points for 1994 vehicles, including at least one in-use vehicle (see the 1994 NFRAQS data point). At the time of testing, the FFV had accumulated approximately 20,000 miles.

During fuel rich operation, particulate emission rates for the FFV were as follows: RFG = 19.9 mg/mi, M85 = 13.1 mg/mi, E85 = 10.7 mg/mi, LPG = 4.2 mg/mi, and CNG = 6.1 mg/mi. Fuel rich testing on RFG, relative to baseline stoichiometric RFG testing, indicates that particulate emission rates increased by about a factor of four during fuel rich operation. The four alternative fuels emitted particulate at rates 30-80 percent lower than Federal RFG. The particulate emission rate on LPG during fuel rich operations was actually less than the baseline stoichiometric emission rate on RFG. Relative (fuel rich) particulate emission rates for the alternative fuels relative to RFG (fuel rich) were as follows: M85/RFG = 0.66, E85/RFG = 0.54, CNG/RFG = 0.31, and LPG/RFG = 0.21.

Mulawa et al. (1997)⁴ report on particulate emission rates for vehicle testing conducted in Alaska as part of a gasoline vs. E10 evaluation program. This research effort was conducted jointly by General Motors, EPA-RTP, ManTech Environmental Technology, the Alaska Department of

Environmental Conservation (ADEC), and the University of Alaska and included testing of one 1994 Ford Aspire and several additional vehicles spanning the 1977-1989 model years. The 1994 vehicle was obtained from a Fairbanks car dealer (odometer reading was 1610 miles) and had been certified to the Federal low temperature CO standard. The paper does not explicitly indicate whether the vehicle was also a Tier I certification, but the certification standards listed for the Aspire in one of the paper's tables imply that it was not.

Particulate testing under the Alaska program was performed at two locations. Testing at ADEC (using an EPA portable FTP setup) was only performed for temperatures of 20°F, 0°F, and -20°F, but testing on a subset of study vehicles at EPA-RTP included standard (75°F) FTP testing as well. Testing at 75°F (on Alaska wintertime commercial gasoline) indicated a particulate emission rate for the Aspire of 1.17 mg/mi and emission rates for two older vehicles tested (a 1987 Plymouth Voyager with 14K miles and a 1989 Chevrolet Celebrity with 16K miles) of 1.55 and 7.51 mg/mi. All three data points are plotted in Figure 2 and the data point for the 1994 Aspire is also included in Figure 4. As indicated, all three are consistent with NFRAQS data points for similar model years, although the 1989 data point is on the low side (perhaps due to the relatively low mileage for a vehicle of such age).

No high temperature testing was performed for the larger EPA/ADEC data set of 10 vehicles, so full range temperature impacts can only be assessed using test results for the three vehicles described above. For these three vehicles, particulate emission rates, as indicated in Table 2, increased by 0-900 percent between 75°F and 20°F, 500-1,800 percent between 75°F and 0°F, and 750-6,000 percent between 75°F and -20°F. It should be noted that although the changes in percentage terms are substantial, all emission rates at all test temperatures were less than the 80 mg/mi Tier I particulate standard for light-duty vehicles. The magnitudes of the percentage change values simply reflect the very low emission rates at 75°F.

Vehicle	Aspire (1994)		Celebrity (1989)		Voyager (1987)	
Percent Increase in Particulate Emissions with Temperature						
Temperature Change	Gasoline	E10	Gasoline	E10	Gasoline	E10
75°F to 20°F	3%	428%	1436%	323%	132%	874%
75°F to 0°F	1491%	1360%	1747%	574%	483%	-100%
75°F to -20°F	1965%	5723%	2785%	1220%	748%	3930%
E10 Particulate Emission Rate Relative to Gasoline Particulate Emission Rate						
75°F	0.34		1.84		0.19	
20°F	1.76		0.51		0.80	
0°F	0.31		0.67		No Data	
-20°F	0.96		0.84		0.91	

Table 2. EPA/ADEC Temperature and Fuel Particulate Relations

Table 2 also indicates the relation between E10 particulate emission rates and those of the baseline gasoline. In almost all cases, emission rates with E10 are lower than those of gasoline. The two exceptions may result from relatively low emission rates on gasoline combined with the large variability of particulate testing as described in Sections 2.1 and 2.2 above. Over all test temperatures, E10 emission rates average about 83 percent of gasoline emission rates.

One interesting aspect of the Alaska test program data is a fairly strong correlation between particulate and HC emission rates (r^2 equals 0.79 for gasoline and 0.89 for E10). Mulawa et al. indicate that this is in contrast to a study performed on high mileage vehicles in Orange County, California⁵. Statistical analysis performed by EEA indicates that the correlation is also in contrast to the NFRAQS and ERC data described above.

The Orange County study referenced by Mulawa et al. was not reviewed for this paper since vehicle selection criteria for the study were not "random." Instead, the 103 vehicles tested for particulate were selected on the basis of high HC and CO emission rates. Similarly, primary particulate emission rates for a study of smoking vehicles in the South Coast Air Quality Management District (SCAQMD)⁶ and a study of high emitting vehicles in Clark and Washoe Counties, Nevada⁷ are also not included in this paper due to intentionally biased vehicle recruitment procedures. The inherent bias of all three of these high emitter studies is toward the determination of older technology vehicle emission rates. All three studies are included in the references for this paper should EPA wish their review (the SCAQMD study is discussed in more detail in Section 3 on particulate size distributions below).

3. PRIMARY PARTICULATE SIZE DISTRIBUTIONS.

The size distribution of primary particulate emissions is of importance in evaluating potential health effects. Since the mid-1980's, particulate matter has been regulated in terms of PM-10, that portion of total suspended particulate with "an aerodynamic diameter less than or equal to a nominal 10 micrometers (μ m)." The NAAQS for particulate was revised from total suspended particulate to PM-10 at that time due to the fact that the latter generally represents the respirable portion of total particulate. Recently, EPA has established an additional NAAQS for particulate of 2.5 μ m or less in recognition of the overall inhalation fraction of particulate in this size range and its ability to penetrate deeply into lung tissue. While this paper does not consider the potential health effects of primary particulate emissions, these size cutoffs are important in determining the properties of light-duty vehicle particulate relative to the various NAAQS.

Measurement of the size distribution of combustion-related particulate is problematic for a number of reasons and these difficulties affect much of the published literature. First, combustion-related particulate is composed of particle chains of highly irregular shape and, as a result, particle "size" has been defined different ways in different studies (e.g., aerodynamic diameter, geometric size, stokes diameter, electrical mobility diameter, equivalent light extinction

diameter). Although the particulate NAAQS is expressed in terms of aerodynamic diameter (determined as the diameter of a unit density, spherical particle which would have the same settling speed as the particulate being measured), this definition does not lend itself well to much of the current fine particulate research. Aerodynamic diameter measurement goes hand-in-hand with mechanical particulate sizing devices (such as cascade impactors), but is less well defined for current fine particle measurement techniques such as electrical mobility analysis.

Recent research has suggested that the number of particles may be equally or more important than particle mass in determining particulate health effects. Therefore, much recent research has focused on the analysis of the very fine particle fraction (0.01-1 μm). The mass of emitted particulate in this size range is significant when compared to larger particles. However, as volume (and mass) increase with the cube of diameter (for the spherical, uniform density particles most often assumed in particulate research), the importance of the fine particle fraction from a particle number standpoint is overwhelming. Unfortunately, due to the sensitivity of measurement methods, research into the submicrometer particle fraction seldom includes corresponding total particulate mass measurements. Mechanical particle sizers such as the cascade impactors used for standard motor vehicle particulate testing cannot resolve particles accurately below about 0.05 μm . Much of the submicrometer research relies on techniques such as electrical mobility analyzers, which in turn cannot resolve particles larger than about 0.8 μm .* As a result, most submicrometer research includes the removal of particles greater than 1 μm prior to size distribution analysis. Unless both (or equivalent) techniques are used

* As indicated, there is significant overlap in the ranges of mechanical and electrical particulate analysis methods. However, a substantial number of submicrometer particles are sized below the lowest level of resolution of mechanical collectors and a significant quantity of particulate mass is contributed by "particles" beyond the measurement range of electrical particles analyzers. As a result, electrical analysis is necessary if finely resolved distributions of submicrometer particulate are desired, while mechanical collection is required to determine total particulate mass.

simultaneously, the utility of submicrometer studies in determining overall particulate mass distributions is limited since the fraction of total mass over 1 μm cannot be determined.

Another important complication of particulate size measurement is that particulate "growth" and loss can occur between sample collection and measurement. Particulate formation involves both nucleation and condensation of gaseous particles (generally in the 0.01-0.1 μm size range) and the agglomeration of particles to form chained particulate. Without proper precautions, both agglomeration and condensation (or volatilization) can continue between sampling and measurement, thereby affecting not only the mass of emitted particulate but the size distribution as well.

As described in Section 2.3, Fanick, et al. (1996)³ at SwRI report particulate test results for one 1994 Ford Taurus FFV certified to California TLEV standards. This study also included an analysis of particulate size distributions for emissions testing on five fuels (Federal RFG, M85, E85, LPG, and CNG), but most testing was performed with the test vehicle operating at fuel rich conditions. Only testing on Federal RFG was also performed for stoichiometric operation to provide a particulate emissions rate baseline. Table 3 summarizes the particulate distribution data from the SwRI study.

Unfortunately, the SwRI study did not include size fractions that correspond directly with either the 10 μm or 2.5 μm cutoffs associated with the particulate NAAQS. However, almost 98 percent of the total particulate mass during stoichiometric vehicle testing had an effective aerodynamic diameter of less than 3 μm , implying that virtually all emitted particulate was PM-10 for the vehicle operated under proper maintenance conditions. The fraction of particulate that is PM-2.5 is more difficult to quantify since the nearest SwRI resolution spans the 2-3 μm range. Assuming uniform distribution of particulate across this range (and correcting for the mass increase of larger diameter particulate) implies an approximate PM-2.5 fraction of 82 percent, but there is no way to determine the actual degree of uniformity of the particle

Test Fuel	Test Condition	Percent of Particulate Mass			
		<3 μ m	<2 μ m	<1 μ m	<0.2 μ m
RFG	Stoichiometry	97.5%	71.1%	71.1%	65.4%
RFG	Fuel Rich	80.4%	66.9%	55.7%	42.9%
M85	Fuel Rich	84.9%	68.9%	56.0%	28.0%
E85	Fuel Rich	97.9%	80.1%	44.5%	30.1%
LPG	Fuel Rich	88.0%	85.6%	80.8%	60.0%
CNG	Fuel Rich	85.5%	67.7%	57.3%	24.9%

Table 3. SwRI Particulate Size Fractions for 1994 TLEV

distribution within this range. Almost no particulate mass is identified between 0.2 μ m and 2 μ m, but over 65 percent of stoichiometric RFG particulate mass is below 0.2 μ m.

The switch to fuel rich operation greatly increased the larger ($>3 \mu$ m) particulate size fraction. This could be due to increased agglomeration associated with both the larger particulate mass emissions rate and a larger number of nucleated particles due to less efficient fuel combustion. Relative to RFG, the alternative fuels tended to have a greater fraction of particulate below 3 μ m, but a greater share of this particulate in the 0.2-2 μ m range.

Durbin et al.⁵ at CE-CERT analyzed the particulate size distributions of 23 light-duty vehicles and trucks operating in the South Coast Air Quality Management District. Although the CE-CERT study targeted smoking vehicles and, therefore, is not a good source of direct information on current technology light-duty vehicles, it does include mass-based particulate distribution data for 22 light-duty vehicles and trucks which can be used to infer certain particle distribution characteristics (at least in terms of bounding ranges) for current technology vehicles. The fraction of measured particulate mass below 10 μ m, 2.5 μ m, and 1 μ m for each of the tested

vehicles in the CE-CERT study is presented in Figure 5. Figure 6 presents a corresponding plot of measured particulate emission rate versus measured PM-1 fraction.

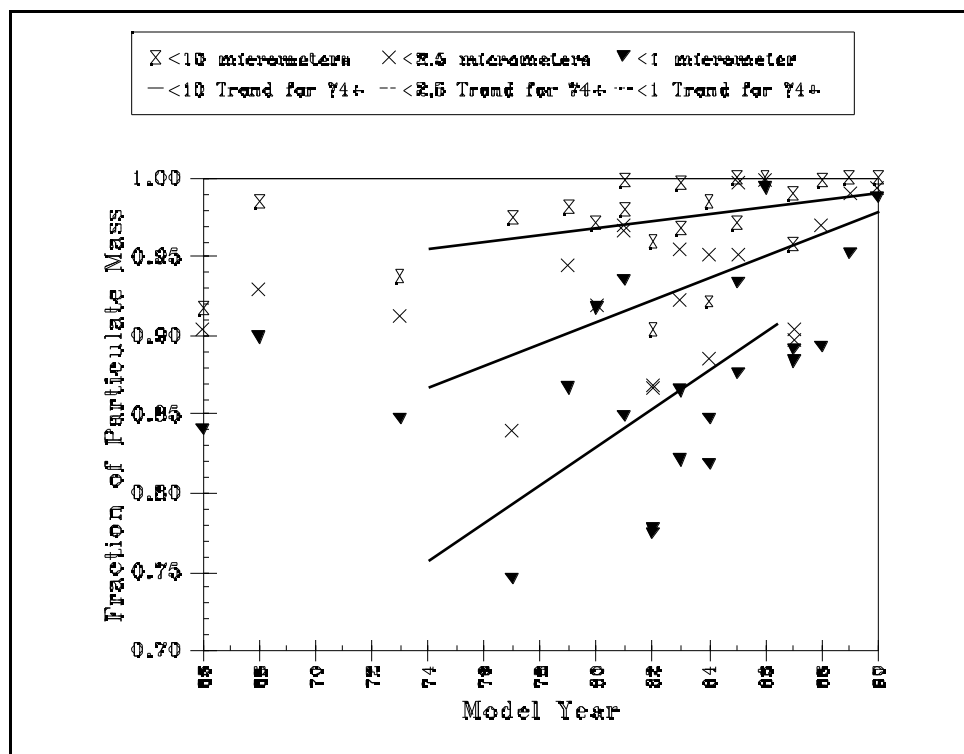


Figure 5. CE-CERT Particulate Fractions by Model Year

A distinct trend toward greater fine particulate mass fractions with increasing vehicle model year is readily observed in Figure 6. Statistically significant trends are observed for increases in PM-10, PM-2.5, and PM-1 when all data is considered. When only catalyst-equipped vehicles are considered, a statistically significant trend for PM-10 is no longer observed, but trends for both PM-2.5 and PM-1 become even more pronounced. For this subset of vehicles, the fraction of particulate that is PM-2.5 increases linearly with model year at a rate of about 0.7 percentage points per year (with 97 percent confidence) between model years 1977 and 1990. The trend for

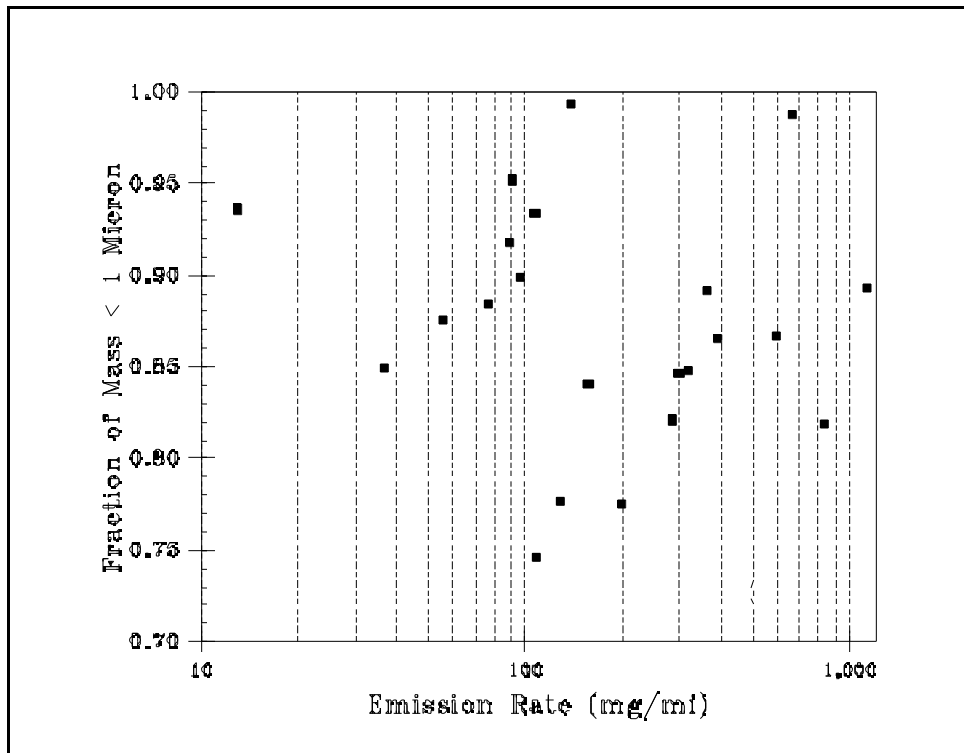


Figure 6. CE-CERT PM-1 Fraction by Particulate Emission Rate

PM-1 is even more pronounced, with the fraction of particulate that is PM-1 increasing linearly with model year at a rate of about 1.2 percentage points per year (with greater than 99 percent confidence) between model years 1977 and 1990.

These observed trends are consistent with a presumption of declining particulate emission rates over time. Generally, as emission rates decline, the number of nucleated and condensed particles available for agglomeration also declines and smaller diameter particulate fractions increase.

However, this presumption does not appear to explain the differences observed in the CE-CERT dataset. Figure 6 illustrates that there is no correlation between measured particulate emission rates and measured PM-1 fraction (that fraction expected to be most sensitive to declining emission rates). Therefore, declining emission rates cannot explain the observed increase in fine particulate fractions. The role of vehicle technology cannot be determined based on the data

presented in the CE-CERT paper, but certainly the lack of emission rate correlation suggests that any such role must affect fundamental particulate formation through some mechanism other than reduced nucleation and condensation sites.

Table 4 presents the average particulate fractions from the CE-CERT dataset. For comparative purposes, statistics are presented for the aggregate dataset as well as specific fuel and vehicle type components. In general, little sensitivity is noted for either PM-10 or PM-2.5, regardless of the subset of test vehicles analyzed. Whether diesel or gasoline, light-duty vehicle or light-duty truck, the average PM-10 mass fraction varies only between 97 and 98 percent of total particulate and the average PM-2.5 mass fraction varies only between 91 and 95 percent of total particulate. Since the impact of individual vehicle anomalies can be magnified for small sample sizes, the variation in calculated averages is also presented separately for samples consisting of more than five vehicles. For these limited samples, the average PM-10 fraction showed essentially no variation, comprising about 97 percent of total particulate mass. PM-2.5 mass fraction variation tightened to 93-94 percent of total particulate and the fraction for PM-1 similarly tightened to 87-89 percent. Caution should be taken in interpreting these restricted sample statistics since diesel vehicles are effectively excluded in their calculation, except when considered in conjunction with gasoline vehicles in an "all vehicle" sample.

Since, the CE-CERT particulate fractions are sensitive to vehicle model year, Table 4 also presents separate particulate fraction averages for 1985-1990 gasoline vehicles and 1966-1984 gasoline vehicles. Here distinct differences are noted, with variations larger than those across either fuel or vehicle type. For the 1985-1990 vehicles, the average PM-10, PM-2.5, and PM-1 mass fractions are 99 percent, 96 percent, and 93 percent respectively. With the exception of PM-10, these values differ substantially from those obtained by SwRI for the 1994 TLEV study described above. While SwRI does not provide explicit fractions for either PM-10 or PM-2.5, their data does indicate that 98-100 percent of particulate mass is PM-10, 71-98 percent is PM-2.5, and 71 percent is PM-1. As described above, assuming a uniform distribution of

Fuel	Vehicle Type	Sample Size	PM-10 Fraction	PM-2.5 Fraction	PM-1 Fraction
Gasoline & Diesel	LDV & LDT	22	0.973	0.934	0.874
Gasoline & Diesel	LDV	15	0.973	0.933	0.865
Gasoline & Diesel	LDT	7	0.974	0.936	0.892
Gasoline	LDV & LDT	17	0.971	0.935	0.885
Gasoline	LDV	12	0.970	0.930	0.870
Gasoline	LDT	5	0.975	0.948	0.920
Diesel	LDV & LDT	5	0.979	0.928	0.835
Diesel	LDV	3	0.984	0.943	0.844
Diesel	LDT	2	0.971	0.907	0.822
Range Over all Sample Subsets			0.970-0.984	0.907-0.948	0.822-0.920
Range Over Subsets with more than 5 Obs			0.970-0.974	0.930-0.936	0.865-0.892
Gasoline	1985-1990	8	0.990	0.963	0.927
Gasoline	1966-1984	9	0.955	0.911	0.848

Table 4. Average CE-CERT Particulate Fractions

particles between 2 and 3 μm in the SwRI study, implies a PM-2.5 fraction of only 82 percent, substantially less than the 96 percent value calculated from the CE-CERT data for 1985-1990 vehicles. Similarly, the 71 percent PM-1 fraction in the SwRI study is over 20 percentage points less than the corresponding value for the CE-CERT study.

It is not possible to resolve these discrepancies based on data presented in either the CE-CERT or SwRI papers. As indicated by the SwRI data for fuel rich operation (and consistent with increased nucleation, condensation, and agglomeration theory), the fraction of particulate that is PM-10, PM-2.5, and PM-1 all decline with increasing particulate emission rates. Yet the

CE-CERT data should be biased toward high emitters as vehicle selection was premised on visible smoke emissions. This bias is reflected in the measured particulate emission rates for the CE-CERT study, which range from 13-1,129 mg/mi (264 mg/mi average) for gasoline vehicles. Contrasted with the 5.5 mg/mi emission rate of the SwRI TLEV, we would expect CE-CERT PM-2.5 and PM-1 particulate fractions to be considerably lower than those of the SwRI study. Exactly the opposite is observed. All three of the CRC study components described in Section 2.2 will include particle size distribution analysis for average in-use light-duty vehicles and trucks. Analysis of this data, when released, may provide insights necessary to explain the observed discrepancy.

Hildemann et al. (1991)⁸ used an electronic aerosol analyzer to determine the submicrometer mass distribution of particulate from seven catalyst-equipped (spanning the 1977-1983 model years) and six non-catalyst light-duty vehicles (spanning the 1965-1976 model years). Exhaust particles greater than 2 μm were mechanically removed before analysis so total particulate emission rates (and overall particulate size fractions) are not known. Given the 220-341 mg of lead per gallon of unleaded gasoline used for the emissions testing for non-catalyst vehicles, the submicrometer particulate emission rates of these vehicles generally were 10-30 times higher than those of catalyst equipped vehicles which were tested using unleaded gasoline. Conspicuously, however, two non-catalyst vehicles exhibited submicrometer emission rates of less than 24 mg/mi, in the same range as the catalyst-equipped vehicles tested.

For catalyst-equipped vehicles, Hildemann et al. found the submicrometer particulate to generally consist of a broad single-mode distribution with a peak between 0.1 and 0.3 μm . For a limited subset of these vehicles, a bi-modal distribution with a second (lower) peak around 0.01 μm was observed. Non-catalyst vehicles generally indicated distribution profiles similar to those of catalyst vehicles (albeit at considerably higher absolute emission rates) with peaks again in the 0.1-0.3 μm range. As was the case for catalyst-equipped vehicles, a second mode was observed

for some non-catalyst vehicles. Testing for a single heavy-duty diesel truck also indicated similar submicrometer distribution characteristics.

Rickeard et al. (1996)⁹ performed both total particulate and submicrometer particulate analysis for four diesel (with and without catalysts) and two gasoline (one non-catalyst) light-duty vehicles over both the European transient test and steady-state test cycles. Unfortunately, full range particle size distributions are only presented for all vehicles in the aggregate and no indication is provided on the degree of variability across vehicles (or fuels). Based on the aggregate data, between 90 and 95 percent of particle mass was PM-10 for testing performed in hot start mode and 88-89 percent of particle mass was PM-10 for testing in cold start mode. For PM-2.5, the corresponding fractions are 85 to 90 percent for hot start testing and about 80 percent for cold start testing. In accordance with similar studies, a distinctive peak in the particle distribution is observed around 0.1 μm .

The particulate size fractions from the Rickeard data are even more inconsistent with the CE-CERT data than those described for the SwRI study above. While vehicle technology may play some role in the discrepancy (the Rickeard test vehicle populations consisted of "typical" European vehicles), it appears that the mass recovery rate of the cascade impactor apparatus was very low and that error was skewed toward the recovery of larger diameter particles. Based on this conclusion, Rickeard abandoned further analysis of the impactor data and focused on submicrometer electrical aerosol analysis. The submicrometer particle analysis generally showed a log-normal particle (number) distribution with a peak around 0.1 μm . Consistent with the other cited studies, particle mass in the submicrometer range peaked between 0.1 and 0.2 μm . These submicrometer relations showed very little sensitivity to test condition, vehicle, or fuel.

Greenwood et al. (1996)¹⁰ performed submicrometer size distribution testing using electrical mobility analysis on two diesel (one with catalyst), three gasoline, and one converted CNG light-duty vehicles. All testing was performed over steady-state cycles. All submicrometer

distributions were log-normal, but peak diameters ranged from 0.03-0.05 μm at idle to 0.02-0.09 μm under load, considerably lower than corresponding values derived in the tests cited above. With one exception, the submicrometer particulate peak for gasoline vehicles was below 0.05 μm for all three vehicles under all test conditions (the exceptional peak was at 0.07 μm). Of the studies reviewed, this is the only one to conclude that "diesel particulates [in the submicrometer range] are larger on average than either gasoline or CNG particulates" (bracketed qualifier added).

4. SECONDARY PARTICULATE EMISSIONS FROM LIGHT-DUTY VEHICLES.

In addition to direct emissions (primary particulate), total ambient particulate loadings include a substantial fraction of solid and liquid material that forms via the atmospheric reaction of gaseous emissions. This so-called secondary particulate is comprised of a large number of chemical components, but the largest contributors generally consist of sulfate- and nitrate-based compounds and secondary organics. Because motor vehicles are significant contributors to ambient organic and oxides of nitrogen (NO_x) emissions, they are also significant contributors to secondary organic and nitrate particulate loadings. Motor vehicle sulfur emissions are not as significant, but do nonetheless contribute to total ambient sulfate. Delucchi and McCubbin (1996)¹¹ have compiled a fairly extensive review of major secondary particulate formation mechanisms and their review coupled with key supplemental studies and clarifying data forms the basis of the secondary particulate material presented in this paper.

Research on secondary particulate formation has been on-going for at least the last three decades and, as a result, the number of research papers available for review far exceeds the resources allocated to this work effort. However, much of secondary particulate research is theoretical in nature and involves the development and subsequent refinement of chemical and mathematical descriptions of complex atmospheric processes. This research tends to be cumulative in that newer papers incorporate and expand on previous work, retaining that which is important and discarding those portions that are outdated. Due to this evolutionary process, newer papers tend to provide a fairly robust synopsis of the cumulative state of research and it is often not

necessary to review an entire chain of research papers to derive an overall assessment of key previous work. This is the general approach taken for this paper and, therefore, although the cited material is ultimately traceable to an original source, it has been extracted for presentation here either from a key original research paper or more often from a secondary "compilation" paper. For this reason, each of the following sections on secondary particulate formation include only generic references to the compilation sources utilized. If desired, each of those listed sources can be consulted for a more extensive list of references to original research papers.

Several researchers have produced empirically-derived estimates of the significance of secondary particulate formation. Generally, these estimates are based on Chemical Mass Balance (CMB) modeling analysis of ambient air monitoring data and rely on the disaggregation of ambient particulate into its source-specific components using best fit statistical procedures in combination with source-specific emissions profiles. Table 5 presents a summary of secondary particulate fractions based on a synopsis of CMB analyses compiled by Delucchi and McCubbin¹¹ and several recent CMB analyses included in an EPA handout prepared for the FACA National and Regional Strategies Workgroup.¹² It is likely that varying levels of accuracy and detail are reflected in the various CMB analyses which comprise the synopsis presented in Table 5 and that significant uncertainty is, therefore, manifest in the estimates. While a detailed review of each component CMB analysis is beyond the scope of this paper, it is obvious that secondary particulate formation contributes a substantial fraction of total ambient particulate and that this fraction is in some cases the single most significant particulate component. To allow the significance of the secondary particulate to be more fully understood, Table 5 also indicates either the fraction of total particulate attributable to primary motor vehicle combustion or combustion from all sources.

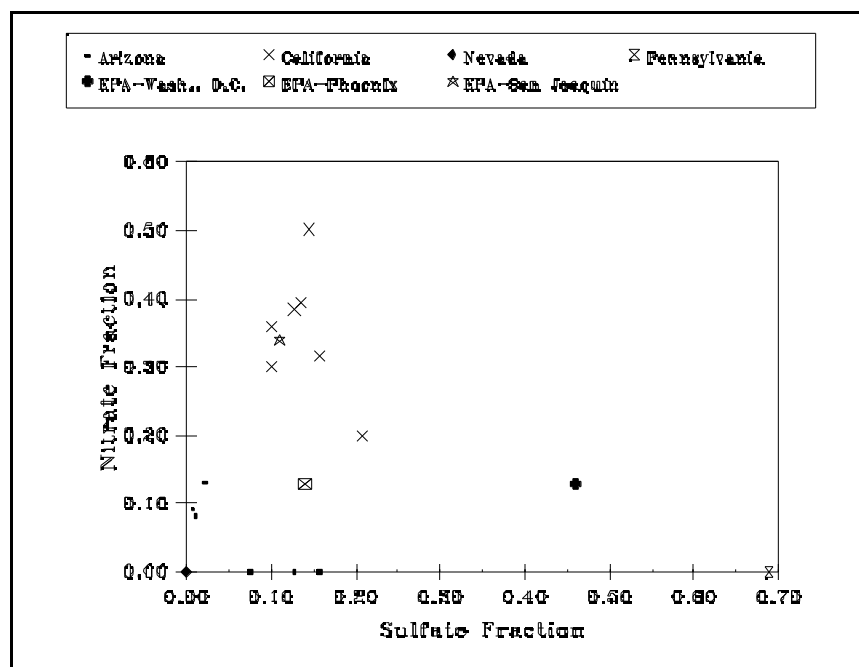
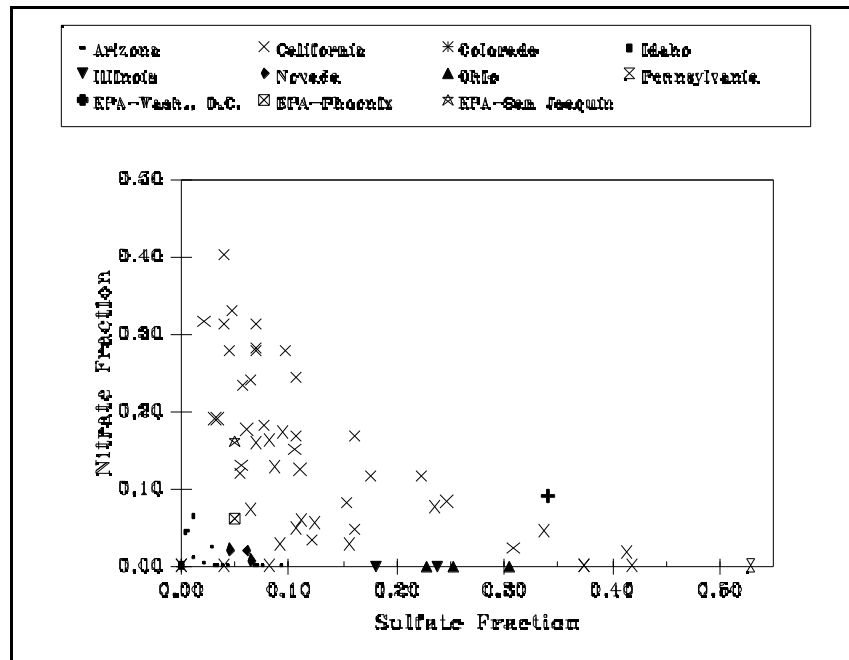
Figures 7 and 8 present a detailed plot of secondary particulate nitrate fractions versus secondary particulate sulfate fractions for each of the individual CMB analyses that comprise the areawide averages presented in Table 5. These figures indicate an obvious inverse relation between

Analysis Location	Number of Analyses	Sulfate Mass Fraction	Nitrate Mass Fraction	Secondary Organic Mass Fraction	Total Secondary Mass Fraction	Primary Vehicle Mass Fraction
PM-10						
Arizona	13	2.7	1.7	n/e ^a	4.4	20.5
California	47	10.2	18.3	n/e	28.5	22.2
Colorado	2	0.0	0.0	n/e	0.0	0.0
Idaho	1	0.0	0.0	n/e	0.0	0.1
Illinois	2	21.8	0.0	n/e	21.8	3.8
Nevada	3	5.7	1.8	n/e	7.5	27.0
Ohio	3	25.6	0.0	n/e	25.6	35.9
Pennsylvania	1	52.8	0.0	n/e	52.8	6.9
EPA-Wash., D.C.	1	34	9	n/e	43	26 ^b
EPA-Phoenix	1	5	6	n/e	11	23 ^b
EPA-San Joaquin	1	5	16	n/e	21	15 ^b
PM-2.5						
Arizona	6	3.5	7.6	0.0	11.1	58.9
California	7	14.0	34.1	7.0	55.1	18.4
Nevada	1	0.0	0.0	0.0	0.0	98.9
Pennsylvania	1	68.8	0.0	0.0	68.8	9.2
EPA-Wash., D.C.	1	46	13	n/e	59	36 ^b
EPA-Phoenix	1	14	13	n/e	27	57 ^b
EPA-San Joaquin	1	11	34	n/e	45	36 ^b

^a n/e indicates that "no estimate" for secondary organic particulate mass was included in the component CMB analyses.

^b Total combustion-related mass fraction.

Table 5. Secondary Particulate Mass Fractions



between secondary sulfate and nitrate particulate (resulting from factors discussed in detail below). Areas of the eastern U.S. tend to exhibit much higher secondary sulfate and much lower secondary nitrate fractions than western areas of the U.S. To better understand this phenomena, the basic physical processes leading to the formation of both secondary particulate sulfate and nitrate is reviewed in greater detail in the following sections.

4.1 Secondary Sulfate Particulate.

Atmospheric sulfate formation results from reactions involving emitted sulfur dioxide (SO₂) with ambient water (H₂O), and oxygen (O₂).^{11,13,14} Motor vehicles contribute to this formation through the combustion-induced reaction of fuel sulfur with oxygen from the air/fuel charge to form SO₂. As a result, the magnitude of motor vehicle contributions to secondary particulate sulfate are directly related to the amount of sulfur present in combustion fuel. There are three major atmospheric removal mechanisms for SO₂ surface retention (dry deposition), precipitation in water (wet deposition), and conversion to sulfuric acid (H₂SO₄). Particulate sulfate formation proceeds from the last of these mechanisms and thus is dependent on the amount of SO₂ that is converted to sulfuric acid.

Sulfuric acid formation proceeds from SO₂ via two reaction pathways summarized as follows:

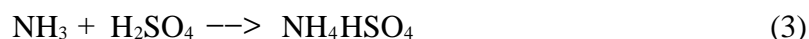


Reaction 1 is a gas phase reaction, limited primarily by the availability of hydroxyl radicals (OH), which are formed during the photochemical oxidation of atmospheric organic compounds.

Although the sulfuric acid formed through reaction 1 is initially gaseous, its vapor pressure is low and it readily condenses onto existing particles or into a liquid droplet. Reaction 2 is an aqueous phase reaction in which SO₂ is initially dissolved in water droplets, which then react quickly with

hydrogen peroxide (H_2O_2) to form sulfuric acid. Relative reaction rates favor reaction 2 by a factor of 10 to 100, but the availability of water droplets is the most important factor in determining the relative importance of the two sulfuric acid production pathways. In many cases reaction 1 predominates, but in instances where relative humidity is high and cloud cover is extensive, reaction 2 can be of equal or greater importance.

Once formed, sulfuric acid is easily neutralized (and thus is relatively rare given sufficient time for neutralization reactions). The primary atmospheric neutralization agent is ammonia (NH_3), but other compounds containing ions such as sodium, potassium, magnesium, or calcium can also act as neutralizers. Most notably, significant sodium-based neutralization can occur in areas with high atmospheric concentrations of sea salt (sodium chloride, NaCl). Ammonia-based neutralization can produce partially neutralized ammonium bisulfate (NH_4HSO_4), partially neutralized tri-ammonium hydrogen di-sulfate ($(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$), or fully neutralized ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). These neutralization reactions are summarized as follows and so long as atmospheric ammonia is not a limiting factor (which in most cases it is not), reaction 4 will be predominant:



Sulfuric acid reactions with ions other than ammonia follow similar hydrogen exchange processes and, as alluded to above, areas with significant atmospheric sea salt can exhibit substantial sodium sulfate (Na_2SO_4) or sodium bisulfate (NaHSO_4) production.

Given the dependencies noted above, the actual mass of aerosol sulfate compounds produced at any given time from a given quantity of SO_2 varies in accordance with several factors, including:

- The rate of photochemical production of hydroxyl radicals and the rate of hydroxyl loss to competing reactions (limiting sulfuric acid production through reaction 1),
- The relative humidity and degree of cloud cover (limiting water droplet availability and, therefore, sulfuric acid production through reaction 2),
- The ambient temperature (through influences on reaction rates),
- The relative locations of SO_2 emission sources and sources of neutralization compounds, and
- The time available for reactions between SO_2 emission and atmospheric measurement.

In all cases, these factors will vary both temporally and geographically and, therefore, it is not possible to state with precision the amount of sulfate formed per unit SO_2 emission unless a specific set of source, receptor, meteorologic, and climatic conditions are defined. On a regional basis, the importance of source location and reaction time can generally be ignored and an SO_2 emissions-removal equilibrium assumed. But equilibrium concentrations will still depend on hydroxyl production, ambient temperature, humidity, cloud cover, and the ratio of neutralizing compound to sulfuric acid concentration.

In most cases, the availability of neutralizing compounds is not a limiting factor in sulfate particulate formation when considered on a regional basis. Significant ammonia emissions derived from such primary sources as livestock operations, biological processes in soil, agricultural operations, domestic pets, and human perspiration generally provide for ambient ammonia concentrations sufficient for complete neutralization on a regional scale¹⁵. Moreover, available neutralizing agents preferentially react with sulfuric acid (when both sulfuric and nitric acids are available) so that sulfate formation generally proceeds to completion before significant quantities

of particulate nitrate are formed. Neutralizing agent availability can, however, be a limiting factor even for sulfate production on a local basis when geographic distinctions between SO₂ and neutralizing agent sources are significant.

For all of these reasons, the estimation of SO₂-to-sulfate conversion rates and resulting particulate sulfate concentrations requires detailed air quality modeling based on accurate descriptions of local conditions. Reviewing results of historical modeling efforts and sulfate formation theory allows some generalizations to be presented, but the applicability of these generalizations to any given set of conditions is unlikely to adequately account for local influences. Therefore, while these generalizations are presented to provide a means of assessing the potential magnitude of sulfate impacts on total atmospheric particulate, any interpretation should be restricted to this purpose.

The sulfuric acid production rate of gas phase reaction 1 has been estimated in a substantial number of research projects over the years and estimates range from a low of 0.01 percent of SO₂ converted per hour, to a high of 10 percent of SO₂ converted per hour (the upper range estimates being applicable to high temperature, high humidity conditions). According to Delucchi and McCubbin, the EPA Office of Policy, Planning and Evaluation has previously assumed a conversion rate of $(0.2 + 0.02P)$ percent per hour, where P is the annual precipitation rate (in inches). Based on the variation in normal annual rainfall throughout the U.S., the EPA relation would imply absolute conversion rates of 0.2-1.5 percent per hour, with a typical value of about 1 percent per hour (generally in the middle of the 0.01-10 percent range noted above).

The total conversion rate of SO₂ to sulfate depends on the reaction rates of both reaction 1 and reaction 2 as well as the rate of dry and wet SO₂ deposition. Various studies have estimated overall SO₂-to-sulfate conversion rates as low as 5 percent and as high as 50 percent, but generally estimates fall in the 10-30 percent range. EPA's Office of Policy, Planning and Evaluation has previously assumed an overall SO₂-to-sulfate conversion rate of 10 percent and

the EPA PART5 emission factor model assumes a 12 percent conversion rate. Recent three-dimensional modeling of the global sulfur cycle estimates a 37-52 percent sulfur conversion rate depending on the speed of aqueous phase reaction 2. Since reaction 2 will only contribute significantly to total SO₂ conversion in areas subject to high humidity and extensive cloud cover, few areas will consistently experience conversion rates on the high end of the range. Obviously, considerable uncertainty exists in this area, but it appears that the conversion rates previously assumed by EPA are on the lower end of the range of current estimates and may underestimate particulate sulfate production, especially in areas of high humidity and extensive cloud cover, such as areas along the U.S. east coast. This conversion rate dependency on water droplet availability is consistent the data presented in Figures 7 and 8 above. It is easily observed from the data presented in these figures that secondary particulate sulfate constitutes a significant fraction of total atmospheric particulate in the few eastern areas where CMB analysis has been performed and, in most cases, a substantially lesser fraction in drier areas. Detailed air quality monitoring analysis of local sulfate to SO₂ concentrations can provide an accurate, empirically-derived assessment of average SO₂-to-sulfate conversion rates for areas and specific time periods of interest.

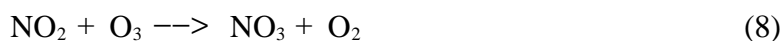
4.2 Secondary Nitrate Particulate.

Atmospheric nitrate formation results from reactions involving emitted NO_x.^{11,14-19} Motor vehicles are major NO_x emitters and, therefore, contribute to nitrate particulate formation. However, due to interrelationships in the photochemical production of ozone and nitrate, the role of NO_x in particulate nitrate formation is quite complex; substantially more so than the role of SO₂ in particulate sulfate formation. The nitrate production cycle begins with the oxidation of nitrogen oxide (NO, which comprises the bulk of NO_x emissions) to nitrogen dioxide (NO₂), nitrogen trioxide (NO₃), and nitrogen pentoxide (N₂O₅).

In the absence of the photochemical production of ozone (O₃), oxidation of NO would occur through reaction with ordinary molecular oxygen (O₂) as follows:



The reaction rate of this oxidation mechanism is comparatively slow, with a half-life for NO of a few days. In the presence of O₃, however, the oxidation of NO is greatly accelerated, and the half-life of NO is reduced to a few minutes, through several reactions, the principal of which are:



As indicated above, it is these reactions which typically dominate NO oxidation and contribute to particulate nitrate formation through the intermediate production of nitric acid (HNO₃).

As was the case for sulfuric acid, there are multiple production pathways in the atmospheric formation of nitric acid, including the following:

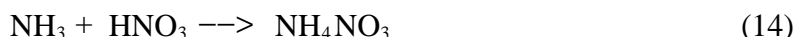




Reactions 10 and 11 are considered to be the most important pathways to particulate nitrate formation, with reaction 10 responsible up to 95 percent or more of nitric acid formation during daytime hours (when photochemical reactions generate the necessary hydroxyl radicals).

Reaction 11 becomes dominant during nighttime hours (when the supply of hydroxyl radicals is insufficient to promote extensive production through reaction 10) and is estimated to be responsible for as much as 80 percent of nighttime nitric acid production.

In a fashion again analogous to the production of particulate sulfate, nitric acid is subsequently neutralized to form particulate nitrate. In the principal neutralization reaction, nitric acid reacts with ammonia to form ammonium nitrate (NH_4NO_3). Sea salt (NaCl) can, however, play a significant neutralization role in areas close to shorelines, generating sodium nitrate (NaNO_3) and hydrogen chloride (HCl) as reaction products. These neutralization pathways are summarized as follows:



The rate at which NO_x is converted to particulate nitrate is substantially more complex than was the case for the conversion of SO_2 to particulate sulfate. All of the factors listed in Section 6.1 which influence the conversion of SO_2 to sulfate (e.g., the production rate of hydroxyl radicals, relative humidity, ambient temperature, source location, and reaction times) also influence the conversion of NO_x . However, additional factors also play significant roles in NO_x conversion.

First, a substantial portion of NO_x is "appropriated" in competing photochemical reactions, most notably involving the production of ozone and peroxyacetyl nitrate (PAN). Second, the ammonia-sulfuric acid particulate production reaction occurs more readily than the ammonia-nitric acid reaction and, therefore, substantial quantities of particulate nitrate will only be produced after the bulk of sulfuric acid has been converted to particulate sulfate. Third, ammonium nitrate readily dissociates back into ammonia and nitric acid. Therefore, the relative concentrations of the three compounds is a function of thermodynamic equilibrium and ammonium nitrate will not accumulate, except to the limits imposed by this equilibrium constraint (nitrates bound to other ions, such as NaNO_3 , are not constrained by this thermodynamic limit, but such nitrate concentrations are generally small except in isolated local situations).

The dissociation constant of ammonium nitrate is high enough to effectively force the equilibrium concentration to zero at temperatures above 100°F , except in cases where significant concentrations of both nitric acid and ammonia are present (20-30 ppb). As relative humidity increases, equilibrium will dictate increased ammonium nitrate production. As temperatures drop below 90°F , significant ammonium nitrate can form even at low to moderate humidity.

Given these various dependencies, the total amount of particulate nitrate formed can vary considerably, especially as control programs are implemented for one or more precursor pollutants (because nitrate formation is dependent on the photochemical ozone cycle, precursor pollutants include not only NO_x and ammonia, but organic gases and, albeit to a lesser extent, CO). Particulate nitrate formation generally decreases with decreases in ammonia (providing sufficient atmospheric ammonia exists to support both sulfuric and nitric acid neutralization), but there is a corresponding increase in the equilibrium concentration of nitric acid which can be important in the context of acid rain.

Decreases in NO_x emissions generally will drive both nitric acid and particulate nitrate concentrations down, but any corresponding increase in ammonia (ammonia increases often occur in direct response to post-combustion NO_x reductions, especially those accomplished through ammonia injection or poorly controlled selective catalytic reduction) can result in the increased rate of conversion of nitric acid to particulate nitrate, offsetting some or all of the expected particulate nitrate reduction. Reductions in organic emissions can produce increases in particulate nitrate formation due to decreases in the amount of NO_x "appropriated" for PAN production. This excess NO_x is then available to participate in both the production of nitric acid and particulate nitrate, effectively resulting in increases in the atmospheric concentrations of both. The net effect may still be beneficial given the health-related aspects of PAN, but it is obvious that determining the net rate of particulate nitrate formation for any given area (or the net impact of a proposed set of emission control strategies) is complex. Typically, detailed air quality modeling based on accurate input of local emissions and meteorology must be performed. Alternatively, as was the case for sulfate particulate, detailed air quality monitoring analysis of local nitrate and total NO_x concentrations can provide an accurate empirically-derived assessment of average NO_2 -to-sulfate conversion rates for specific areas and time periods of interest.

Gray and Kuklin¹⁸ have performed detailed atmospheric modeling and air quality monitoring analysis of nitrate formation for various regions of the U.S. Figure 9 summarizes the NO_x -to-particulate nitrate conversion rates estimated by Gray and Kuklin. As indicated, conversion rates range from near zero to a maximum of about seven percent. Conversion rates tend to be highest along the Pacific coast and all regions show similar seasonal variations, with maximum conversion occurring during the spring. On an annual average basis, conversion rates range from about 0.5-4 percent. The number of specific factors influencing observed regional relationships renders a detailed analysis beyond the scope of this paper, but these factors have been described in general terms above. The lowest NO_x conversion rates would be expected in areas with significant SO_2 emissions, high humidity, extensive cloud cover, and low ammonia emissions. These factors combine to promote extensive SO_2 conversion using much (or all) of

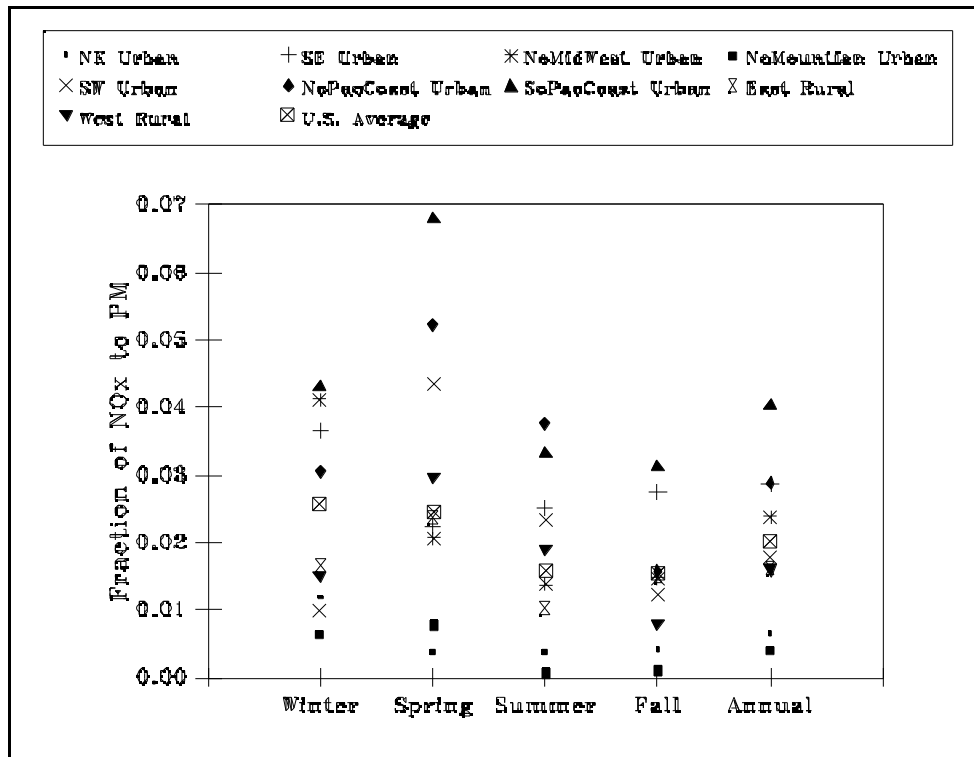


Figure 9. NO_x-to-PM Nitrate Conversion Fractions

available ammonia emissions and, thereby, limit the thermodynamic equilibrium concentration of particulate nitrate. Most regions of the eastern U.S. exhibit meteorological conditions conducive to high SO₂ conversion rates, thereby inhibiting NO_x conversion. While only a generalization, this phenomena agrees well with the conversion rate trends illustrated in Figure 9. This inverse relationship between particulate sulfate and particulate nitrate formation is perhaps best illustrated in Figures 7 and 8, where it is clearly shown that areas with substantial particulate sulfate conversion tend to have only limited particulate nitrate conversion (and vice versa).

DeLucchi and McCubbin assume a 5-7 percent NO_x-to-nitrate conversion rate and attribute a five percent conversion rate to previous EPA work. The work of Gray and Kuklin implies that such conversion rates are high by a factor of about two on a U.S.-average basis, regardless of season.

In fact, only along the Pacific coast is a conversion rate of five percent ever achieved and then, only during the springtime. Given the empirical basis of the Gray and Kuklin estimates (which are derived from ambient air monitoring data), a reasonable accuracy seems likely. Nevertheless, there are issues associated with particulate nitrate measurement which can lead to error in calculating conversion rates from empirical data.

As indicated above, particulate nitrate production is very sensitive to thermodynamic equilibrium. Unless carefully controlled, particulate nitrate dissociation into gaseous nitric acid and ammonia can occur between sample collection and analysis. Conversely, some mechanical collection filter mediums have been shown to promote additional nitrate particulate formation through the absorption and neutralization of nitric acid. While it is assumed that sufficient quality control was observed in the collection and analysis of the data upon which the Gray and Kuklin estimates were based, there is no way to provide independent confirmation within the scope of this paper.

4.3 Secondary Organic Particulate.

While organic particulate comprises the bulk of primary (i.e., emitted) particulate matter, some additional fraction of gaseous organic emissions also undergoes condensation or subsequent reaction in the atmosphere to form secondary particulate matter.^{11,13,22-26} Research into secondary organic particulate has advanced considerably over the years and fairly robust "fractional aerosol coefficients" have been developed and refined for most important secondary organic species. EEA was not tasked to investigate secondary organic particulate as part of the work assignment associated with this paper and, therefore, no detailed discussion on secondary organic formation is presented. In general, the most important contributors to secondary organic particulate formation are olefins, aromatics, cyclic olefins, phenols, and terpenes, and the overall contribution of secondary organic particulate to total ambient particulate tends to be much less

than either secondary sulfate or nitrate particulate (see Table 5). Key recent references, as indicated above, have been included to allow more in-depth review if desired by EPA.

5. SECONDARY PARTICULATE SIZE DISTRIBUTIONS.

As discussed in Section 3, the size distribution of atmospheric particulate is important in evaluating potential health effects. This is as true for secondary particulate as it is for primary particulate. Equally true is the fact that the measurement of secondary particulate size distributions is as, or more, problematic than corresponding measurements for primary particulate. As discussed in Section 3, potential problem areas in the measurement of primary particulate include:

- Differing methods of classifying particle size,
- Differing measurement parameters (particulate number vs. particle size),
- Lack of a single measurement technique capable of resolving the full range of particle size, and
- Sample instability between collection and analysis.

Each of these problem areas, with the possible exception of that of a full range measurement technique, are equally applicable to secondary particulate analysis. Secondary sulfate and nitrate particulate tends to be somewhat larger in effective diameter than primary organic particulate (where size distribution peaks of 0.1-0.2 μm are evident), thereby facilitating the use of mechanical collectors (such as cascade impactors) to resolve secondary sulfate and nitrate particulate distributions over the full range of particle size. This exception does not hold for secondary organic particulate where, like primary organic particulate, the bulk of particles will be below 1 μm in effective diameter.

As was also the case with primary particulate, sampling location and timing are important factors in the determination of secondary particulate size distributions. Agglomeration of smaller

particles is an important aspect of particulate formation and, therefore, over time (and space) particle size distributions can vary as agglomeration becomes either more, or less, significant. Therefore, size distributions developed in one area or for one time may not be entirely consistent with distributions in other areas or even the same area at another time. For primary motor vehicle particulate this consistency issue is "solved" by specifying a standard dilution tunnel construction and sampling procedure. No such standard can exist for secondary particulate as sampling must obviously occur at the ambient location of interest and reflect the actual particulate formation influences of that location. It is important to note that the standardization of primary motor vehicle particulate sampling does not affect continued post-combustion agglomeration in the atmosphere after measurement, but does provide for a standard measurement of motor vehicle primary particulate at one point in time and space. As a result, primary particulate size distributions determined via standard FTP sampling and analysis may reflect a larger fine particulate fraction than would be observed at some point downstream in the atmosphere after extended opportunity for agglomeration had occurred.

Despite these potential problem areas, research has been undertaken to define secondary particulate size distributions. John et al.²⁰ found that both secondary sulfate and nitrate particulate exhibit well defined tri-modal log-normal distributions with peaks of about 0.2 μm , 0.7 μm , and 4-5 μm . The smallest of the modes is considered to reflect homogeneous gas phase nucleation products as described in the preceding sections, while the larger submicrometer mode is considered to reflect both aqueous phase (i.e., droplet) reaction products and agglomeration of smaller condensation products. The largest mode tends to be the broadest mode and is considered to reflect both continued particle agglomeration and larger particles formed through reactions with ions such as sodium, calcium, or magnesium.

In the case of secondary sulfate particulate, the 0.7 μm mode was consistently shown to be dominant, while the dominant mode for secondary nitrate particulate exhibited a diurnal sensitivity, with the 0.7 μm mode dominating from early morning to mid-afternoon and the super-micrometer mode dominating for the remaining hours. Given this time dependency, the

determination of a single size distribution for secondary particulate nitrate is obviously problematic (even if the additional problems cited above are ignored).

While John et al. classified particle concentrations by mode, they did not quantify that fraction of particulate below applicable NAAQS (or any other) size cutoffs. However, given the observed particle distribution modes, a rough approximation of the size fractions below NAAQS cutoffs can be made by assuming that all particles associated with the two submicrometer modes are below 2.5 μm in effective diameter and that particles associated with the larger mode are greater than 2.5 μm . There is certainly some error associated with such assumptions since a tail of the larger submicrometer mode distribution extends out beyond 2.5 μm and a tail of the largest mode distribution extends into the sub-2.5 μm range. However, these are opposing errors and since, on the basis of plots presented in the John paper, each appears to be small, the assumption should provide for reasonable accuracy. On the basis of these same plots, it appears that some fraction of both secondary sulfate and nitrate particulate mass is above 10 μm in effective diameter, but that this fraction is small and on the order of a few percent.

Given these assumptions and the concentration data presented by John et al. for each of the three secondary particulate mode distributions, it appears that approximately 68 percent of secondary particulate nitrate is PM-2.5 during the summer and 89 percent is PM-2.5 during the fall. The corresponding distributions for secondary particulate sulfate are 84 percent during the summer and 91 percent during the fall. It is not clear how these distribution would be affected in other geographic areas (the analysis reported by John et al. was for southern California). Since the data presented by John et al. reflects mean seasonal distribution characteristics, the PM-2.5 fraction for secondary nitrate presumably reflects the mean effect of the diurnal sensitivity noted above.

Delucchi and McCubbin¹¹ compiled secondary sulfate and nitrate particulate size distribution data from other studies and found a considerable range of reported PM-2.5 fractions. Reported

fractions for secondary sulfate particulate were less variable and generally ranged from 90-97 percent, but reported PM-2.5 fractions for secondary nitrate particulate ranged from a low of 12 percent to a high of 90 percent. Delucchi and McCubbin assume a PM-2.5 fraction of 95 percent for secondary sulfate particulate and 80 percent for secondary nitrate particulate. Although a bit high for secondary sulfate particulate, the Delucchi and McCubbin fractions are generally in good agreement with the fractions reported by John et al., especially given the range of values on which they based their assumptions.

Obviously there is considerable variability in the range of secondary particulate size distributions reported to date. It seems unlikely that locality- or temporal-specific conditions can account for the wide range of variation in reported secondary particulate size. More likely is that some measurement uncertainty, due to one or more of the issues described above, is also inherent in reported data. It is not possible to resolve these potential impacts with the scope of this paper, but it appears that (at least in most instances):

- 85-95 percent of secondary sulfate particulate is PM-2.5 and all but a few percent is PM-10.
- 70-90 percent of secondary nitrate particulate is PM-2.5 and all but a few percent is PM-10.

6. REFERENCES.

1. Environmental Research Consortium, "Current Vehicle Particulate Emissions Characterization Project", Attachment 30 to comments submitted by the American Automobile Manufacturers Association to Docket Nos. A-95-54, A-95-58, A-95-38, and A-96-51 for revisions to the ozone and particulate matter NAAQS, March 12, 1997.
2. "Measurement of Exhaust Particulate Matter Emissions from In-Use Light-Duty Motor Vehicles in the Denver, CO Area", progress report on CRC Project E-24-1, June 16, 1997.
3. Fanick, E.R., Whitney, K.A., Bailey, B.K., "Particulate Characterization Using Five Fuels", SAE paper 961089, presented at the 1996 International Spring Fuels & Lubricants Meeting, Dearborn, MI, May 6-8, 1996.
4. Mulawa, P.A., Cadle, S.H., Knapp, K., Zweidinger, R., Snow, R., Lucas, R., Goldbach, J., "Effect of Ambient Temperature and E-10 Fuel on Primary Exhaust Particulate Matter Emissions from Light-Duty Vehicles", *Environ. Sci. Technol.*, 31: 1320-1307, 1997.
5. Mulawa, P.A., Cadle, S.H., Sagebiel, J., Zielinska, B., Walsh, P., Chow, J., Knapp, K., Zweidinger, R., Snow, R., "Particulate and Speciated Hydrocarbon Emission Rates from In-Use Vehicles Recruited in Orange County, CA", submitted for publication in *Environ. Sci. Technol.*
6. Durbin, T.D., Smith, M.R., Norbeck, J.M., Truex, T.J., "Population Density, Particulate Emission Characterization, and Impact of the Particulate Inventory of Smoking Vehicles in the South Coast Air Quality management District", submitted for publication in the *J. Air Waste Manage. Assoc.*
7. Sagebiel, J., Zielinska, B., Walsh, P., Chow, J., Cadle, S.H., Mulawa, P.A., Knapp, K., Zweidinger, R., Snow, R., "PM₁₀ Dynamometer Exhaust Samples Collected from In-Use Service Vehicles in Nevada", in press in *Environ. Sci. Technol.*
8. Hildemann, L.M., Markowski, G.R., Jones, M.C., Cass, G.R., "Submicrometer Aerosol Distributions of Emissions from Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat Cooking Operations", *Aerosol Sci. Technol.*, 14: 138-152, 1991.
9. Rickeard, D.J., Bateman, J.R., Kwon, Y.K., McAughey, J.J., Dickens, C.J., "Exhaust Particulate Size Distribution: Vehicle and Fuel Influences in Light Duty Vehicles", SAE paper 961980, presented at the 1996 International Fall Fuels & Lubricants Meeting & Exposition, San Antonio, Texas, October 14-17, 1996.

10. Greenwood, S.J., Coxon, J.E., Biddulph, T., Bennett, J., "An Investigation to Determine the Exhaust Particulate Size Distributions for Diesel, Petrol, and Compressed natural Gas Fuelled Vehicles", SAE paper 961085, presented at the 1996 International Spring Fuels & Lubricants Meeting, Dearborn, MI, May 6-8, 1996.
11. Delucchi, M.A., McCubbin, D.R., "The Contribution of Motor Vehicles and Other Sources to Ambient Air Pollution", UCD-ITS-RR-96-3 (16), Institute of Transportation Studies, University of California, Davis, August 1996.
12. U.S. Environmental Protection Agency, *PM-2.5 Composition and Sources*, handout prepared for the FACA National and Regional Strategies Workgroup, June 16, 1997.
13. Pilinis, C., Farber, R.J., "Evaluation of the Effects of Emission Reductions on Secondary Particulate Matter in the South Coast Air Quality Basin of California", *J. Air Waste Manage. Assoc.*, 41: 702-709, 1991.
14. Kennedy, I.R., *Acid Soil and Acid Rain: The Impact on the Environment of Nitrogen and Sulphur Cycling*, Research Studies Press Ltd., Letchworth, England, 1986.
15. Russell, A.G., McRae, G.J., Cass, G.R., "Mathematical Modeling of the Formation and Transport of Ammonium Nitrate Aerosol", *Atmospheric Environment*, 17: 949-964, 1983.
16. National Research Council, *Nitrates: An Environmental Assessment*, National Academy of Sciences, Washington, D.C., 1978.
17. Perkins, H.C., *Air Pollution*, McGraw-Hill, New York, NY, 1974.
18. Gray, H.A., Kuklin, A., *Benefits of Mobile Source NO_x Related Particulate Matter Reductions*, SYSAPP-96/61, Systems Applications International, San Rafael, California, October, 1996.
19. Russell, A.G., Cass, G.R., "Verification of a Mathematical Model for Aerosol Nitrate and Nitric Acid Formation and Its Use for Control Measure Evaluation", *Atmospheric Environment*, 20: 2011-2025, 1986.
20. John, W., Wall, S.M., Ondo, J.L., Winklmayr, W., "Modes in the Size Distributions of Atmospheric Inorganic Aerosol", *Atmospheric Environment*, 24A: 2349-2359, 1990.
21. Russell, A.G., McCue, K.F., Cass, G.R., "Mathematical Modeling of the Formation of Nitrogen-Containing Pollutants. 2. Evaluation of the Effect of Emission Controls", *Atmospheric Environment*, 22: 1336-1347, 1988.

22. Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C., Seinfeld, J.H., "Gas/Particle Partitioning and Secondary Organic Aerosol Yields", *Environ. Sci. Technol.*, 30: 2580-2585, 1996.
23. Bowman, F.M., Pilinis, C., Seinfeld, J.H., "Ozone and Aerosol Productivity of Reactive Organics", *Atmospheric Environment*, 29: 579-589, 1995.
24. Pandis, S.N., Wexler, A.S., Seinfeld, J.H., "Secondary Organic Aerosol Formation and Transport -- II. Predicting the Ambient Secondary Organic Aerosol Size Distribution", *Atmospheric Environment*, 27A: 2403-2416, 1993.
25. Pankow, J.F., "An Absorption Model of Gas/Particle Partitioning of Organic Compounds in the Atmosphere", *Atmospheric Environment*, 28: 185-188, 1994.
26. Zhang, S.H., Shaw, M., Seinfeld, J.H., Flagan, R.C., "Photochemical Aerosol Formation From α -Pinene- and β -Pinene", *Journal of Geophysical Research*, 97: 20,717-20,729, 1992.

Attachment 1

**ERC Particulate Data
Included in the
AAMA Comments on the
Ozone and Particulate Matter NAAQS**

Current Vehicle Particulate Emissions Characterization Project

Purpose

This project shall address the need to obtain primary exhaust particulate emissions data on current late model light-duty gasoline vehicles.

Target Vehicles

The fleet will consist of 5 of each manufacturer's late model vehicles--light-duty trucks and cars--representative of the high volume models or engine families. It is desirable that the initial mileage be in the range of approximately 4K miles. A high mileage fleet (approx. 100K) will also be tested.

Particulate Measurements and Chemical Characterization

Total exhaust particulate matter collected isokinetically from the dilution tunnel would be weighed to determine mass emission rates. Analysis of the carbon fraction and metals is anticipated at sites where additional filter collection capacity exists. Pallflex T60A20 and Gelman Teflo filters (2 μ m pore size) will be used for mass and metals determination. Pallflex Quartz (2500QAT-UP) will be used for carbon determination. Possible additional work on particle sizing using cyclones, impactors or the MOUDI instrument, if available, would be valuable.

Driving Cycle and Testing Protocol

The 1975 FTP driving schedule will be used during the program. The test protocol shall be as follows. In order to collect sufficient mass to be measureable, separate samples for each of the 3 phases will be collected over four (4) consecutive cold start tests. Background or diluent air samples will be collected similarly. Fifty percent of the fleet will be tested in replicate.

Fuel

Howell California Phase II fuel (CFII) will be used for all testing as this fuel is judged to be the most stable, in terms of formulation, and likely to remain available for the next few years.

ERC Vehicle Fleet Key

<u>Vehicle code</u>	<u>Manufacturer</u>	<u>Model</u>	<u>MY</u>	<u>Engine L.</u>
A	Ford	Town Car	96	4.6
B	General Motors	Cutlass	96	3.1
C	General Motors	Olds LSS	95	3.8
D	General Motors	Grand Am	94	2.3
E	Ford	F-150	97	4.2
F	Ford	Windstar	96	3.8
G	Chrysler	Full Pick-up	98	5.2
H	Chrysler	Sport utility	97	4.0
I	General Motors	Silhouette	95	3.8
J	General Motors	Lumina APV	94	3.1
K	General Motors	LeSabre	94	3.8
L	General Motors	Corvette	94	5.7
M	General Motors	Park Avenue	94	3.8
N	Chrysler	Sport utility	97	4.0
O	Chrysler	Full Pick-up	98	5.2
P	General Motors	S-10	95	4.3
Q	Ford	Taurus	96	3.0
R	Ford	Escort	96	1.9
S	Ford	Explorer	96	4.0

Environmental Research Consortium Low Mileage Vehicle Fleet Emissions Summary

Vehicle		MY	Engine disp. L	Fuel delivery	Test Fuel	Odometer miles	HC	CO (g/mi)	NOx	PM (mg/ml)			Weighted	
											Phase 1	Phase 2	Phase 3	
CARS														
A	1996	4.6	MFI	CA Phil	<6K		0.09	0.91	0.06	0.89	0.67	0.54	0.68	
B	1996	3.1	SFI	CA Phil	6614		0.20	1.72	0.37	0.68	0.84	1.05	0.86	
C	1995	3.8	SFI	CA Phil	6680		0.21	1.74	0.38	0.76	0.48	0.30	0.49	
D	1994	2.3	PFI	CA Phil	15131		0.14	1.25	0.27	1.30	0.60	0.45	0.71	
				CA Phil	5327		0.13	1.49	0.14	0.71	0.25	0.60	0.44	
Q	1996	3.0	MFI	CA Phil	5378		0.11	1.66	0.15	0.68	0.96	0.30	0.72	
R	1996	1.9	SFI	CA Phil	5346		0.14	1.16	0.14	1.77	0.36	0.64	0.73	
				CA Phil	5656		0.07	1.08	0.08	0.43	0.12	0.30	0.23	
MEAN							0.13	1.28	0.18	0.97	0.50	0.51	0.60	
STD DEV							0.04	0.28	0.11	0.44	0.20	0.13	0.17	
TRUCKS														
E	1997	4.2	SFI	EEE	<8K		0.12	1.00	0.04	7.55	0.15	1.29	1.98	
				EEE	<8K		0.12	1.00	0.04	6.31	0.11	1.65	1.81	
F	1996	3.8	MFI-SPI	EEE	<8K		0.11	0.87	0.13	4.56	0.17	0.62	1.2	
G	1998	5.2	SFI	EEE	5933		0.29	3.26	0.37	3.20	2.06	1.99	2.28	
				EEE	6069		0.34	3.83	0.37	2.29	1.61	1.95	1.85	
H	1997	4.0	SFI	EEE	2514		0.14	0.75	0.16	1.85	1.88	2.66	2.09	
				EEE	2569		0.16	0.86	0.18	1.60	1.11	2.01	1.46	
I	1995	3.8	SFI	CA Phil	10901		0.17	1.74	0.42	0.75	0.60	0.60	0.63	
				CA Phil	11271		0.15	1.76	0.37	1.50	0.24	0.00	0.43	
J	1994	3.1	EFI	CA Phil	36201		0.29	4.31	0.69	1.44	0.61	0.60	0.78	
S	1996	4.0	SFI	CA Phil	5461		0.09	1.06	0.08	0.90	0.10	0.29	0.32	
MEAN							0.18	1.91	0.27	2.78	0.68	1.08	1.22	
STD DEV							0.08	1.33	0.21	2.06	0.65	0.77	0.65	

Environmental Research Consortium High Mileage Vehicle Fleet Emissions Summary

Vehicle	MY	Engine disp. L	Fuel	Test Fuel	Odometer miles	HC	CO (g/mi)	NOx	PM (mg/mi)					
										Phase 1	Phase 2	Phase 3	Weighted	
CARS														
K	1994	3.8	SFI	CA Phil	89992	0.16	0.94	0.44	1.90	0.69	0.58	0.91		
L	1994	5.7	PFI	CA Phil	89978	0.24	2.46	0.56	2.28	0.25	0.76	0.81		
M	1994	3.8	SFI	CA Phil	100000	0.17	1.84	0.30	1.77	0.32	0.59	0.7		
MEAN						0.19	1.75	0.43	1.98	0.42	0.64	0.81		
STD DEV						0.036	0.62	0.11	0.22	0.19	0.08	0.09		
TRUCKS														
N	1997	4.0	SFI	CA Phil	99535	0.21	1.51	0.20	1.44	0.69	1.37	1.03		
O	1998	5.2	SFI	CA Phil	99587	0.21	1.58	0.20	2.41	0.74	2.16	1.47		
				CA Phil	119168	0.22	3.03	0.42	3.69	0.88	2.18	1.82		
P	1995	4.3	CPI	CA Phil	61800	0.50	4.00	0.52	4.62	0.74	1.36	1.72		
MEAN						0.31	2.86	0.38	3.41	0.78	1.77	1.60		
STD DEV						0.13	1.01	0.13	1.12	0.07	0.33	0.25		

Attachment 2

**NFRAQS Particulate Study
Progress Report for June 1996**

Measurement of Exhaust Particulate Matter Emissions from In-Use Light-Duty Motor Vehicles in the Denver, CO Area

Progress Report
CRC Project E-24-1
June 16, 1997

Summer study

All of the filter analyses for the summer portion of the study have been completed by DRI except the determination of hopanes and steranes. Results have been transmitted to study participants and analysis has been reinitiated.

Six filters collected during the summer study had flow problems due to filter plugging. It had been hoped that the total carbon results from the corresponding quartz filters, which did not experience plugging, could be used to improve the estimated mass emission rate for these samples. Unfortunately the correlations between total carbon (TC) and mass are not good enough to permit the use of the data in that manner. Therefore, these will be flagged as estimates in the final report.

Attachment 1 shows the correlation between TC and mass for all filters analyzed. The slope of the regression line is close to 1.0, but would be expected to be close to 0.8 using conventional wisdom and logic (i.e. all the mass can't be carbon, there must be H, some O, S, N, other trace elements, and possibly water). The large number of values where TC is much higher than mass is difficult to explain, but has been observed in other work we have done with DRI. Possible explanations include 1) inhomogeneous filter samples. Only a small portion of the filter is analyzed for carbon. Some filters were visually inhomogeneous, but these were avoided in the samples sent to DRI. Analysis of multiple punches from 3 filters did not show major problems, but the result is not definitive. 2) Adsorption of OC on the filters, which is known to occur, could cause high results. Analysis of backup filters does show some adsorption, but this data set is also not very definitive. 3) Sampling problems with either the Teflon (mass) filter or the quartz filter. Earlier QA did not indicate any problems. Additional analyses involving multiple punches of filters and quartz backup filters behind both Teflon and quartz filters will be conducted on the winter samples to see if we can obtain a more definitive explanation for these observations.

Attachment 2 is a Table giving the % organic carbon (%OC) and elemental carbon (%EC) by phase for each of the FTP runs analyzed. Samples are sorted by category - i.e. diesel, 1971-80 vehicles, etc. Note that diesels have the lowest %OC of all the categories. Smokers have %OC values as high as 99%. These results agree with visual observation which showed some of the smoker samples as having a light yellow appearance, compared to the jet black appearance of most the other filters, especially the diesels. In several categories there is a trend to having the highest %OC associated with phase 2 of the FTP.

Attachment 3 shows a PAH profile generated by DRI comparing the results for all gasoline vehicles in this study (labeled average) with only the high emitter and smoking gasoline vehicles in this study (labeled average HS) and with results obtained for IM240 samples from high emitting vehicles in the CAWRSS study (labeled CAWRSS). Profiles are similar. Note, however, that the data is on a log scale, which tends to minimize differences.

Attachment 4 shows the ratio of total dimethylphenanthrenes to total PAH (gaseous plus particulate phase with naphthalene excluded due to blank problems) for each of the samples. L, M, H, S, and D stand for low, medium, high, smoker, and diesel sample respectively. Note that for these compounds there are significant differences by FTP phase and between emitter categories. Thus, it may be a challenge to

provide an in-use whole fleet profile for some compounds.

Attachment 5 shows the dimethylphenanthrenes as their %OC. This profile gives a somewhat different impression than that given in attachment 4, where diesels had a relatively high ratio. Similar plots have been prepared for other compounds.

Sulfate and nitrate emission rates were determined for 34 gasoline vehicles. Only one had a sulfate emission rate higher than 1 mg/mi. The same vehicle had the highest nitrate emission rate, 0.17 mg/mi. Comparison of sulfate emission rates to total sulfur emission rates determined by XRF showed that there is considerably more sulfur present than can be accounted for by sulfate. Presumably much of the sulfur remains present as organo sulfur compounds. Sulfate emissions were somewhat higher from the four diesel vehicles tested, averaging 5.6 mg/mi but ranging from 1.1 to 17.8.

Other elements determined by XRF that appear to have significant emission rates include Zn, P, Ca, Mg, Cu, Fe, Al, Si, and Cl. These will be examined in more detail later.

Winter Study

QA/QC checks on the winter study mass samples have, for the most part, been completed. Repeated weightings of control filters in the field had a standard deviation of 6 ug. This is a worse case figure since these filters were kept in a closed dish (i.e. not always in equilibrium with the room air) and took much longer to come to weighing equilibrium than the sample filters that were left partially open to the room air. Tunnel blanks were found to be higher in the winter study than the summer, probably because there was greater mixing of low and high emitters during the winter than the summer. FTP equivalent tunnel blanks were on the order of 1 mg/mi. Duplicate filters collected side-by-side showed good agreement on the EPA site, but had some problems on the CDPHE site, indicating that there may have been a problem at some point with the quartz filters on the CDPHE site. To date, those filters have not been used, and thus we have not tried to resolve this potential problem.

A comparison was done on PM emission rates for the vehicles tested indoors and outdoors (i.e. CDPHE vs. EPA) by FTP phase. Correlations were poor, but averages were in good agreement. For gasoline vehicles phases 1-3 on the EPA site averaged 548, 74, and 79 mg/mi. For the same phases on the CDPHE site they were 267, 63, and 84 mg/mi. Only phase 1 shows a significant difference, which was expected since the EPA site was run outdoors at prevailing low temperatures while the CDPHE site was operated indoors at 60 F. IM240 results for all vehicles averaged 269 mg/mi on the CDPHE site and 288 mg/mi on the EPA site.

Attachment 6 gives the FTP emission rates from replicate tests in both the summer and winter. Results are judged to be reasonable considering that the first test is on the vehicle as received. Attachment 7 gives the results of the back-to-back IM240 tests for the winter. Again, results are generally reasonable.

Samples were selected for analysis and shipped to DRI. Samples collected outdoors were chosen since that is the most realistic test. 42 complete three phase FTP filter sets were selected. All filters in these sets will be analyzed for OC/EC by TOR, trace elements by XRF, and sulfate and nitrate by IC. GC/MS analysis of PAHs will be performed on composite samples. 11 diesel runs are composited into 5 sets, 8 smokers into 3 sets, 6 low emitters into 2 sets, 5 mid-low emitters into 2 sets, 8 medium emitters into 3 sets, and 4 high emitters into 2 sets. Sets consist of the three FTP phases. In addition, 18 indoor phase 1 FTP samples will be analyzed by TOR, XRF, and IC to compare to the outdoor samples. It is assumed that any significant differences should show up in phase 1 rather than phases 2 and 3. 8 sets of Teflon/quartz back-to-back filter pairs along with simultaneously collected quartz/quartz back-to-back filter pairs will be analyzed for additional information on OC adsorption.

DRI has promised that most of the samples will be analyzed by July 1st. The last batch of samples to be

sent will be analyzed in mid-July, and thus the complete data set should be available to us by mid August. PAH data will be available by the end of June. Hopane and sterane analyses from both the summer and winter studies will be completed in July.

General

Samples for the determination of contemporary carbon content were selected and sent to NIST, which is performing the analyses under separate CRC contract. A total of 5 samples each containing 9 filters (3 phases of 3 FTPs) were selected. Two additional samples were sectioned into halves and sent to DRI and NIST for a carbon methods comparison that will include analysis of multiple punches for each filter.

As a result of Rick Barrett's presentation on smoking vehicles at the CRC workshop, we were approached by Gary Bishop, who is willing to examine a Denver remote sensing data set for the presence of smoking vehicles. Smoking vehicles are sensed by reductions in the remote sensor reference beam caused by light scattering and adsorption. The cost to the program is approximately \$2000. Since this can be accommodated within the current budget, we have authorized DU to proceed with the analysis.

The contract employee who was performing much of the data analysis on this program secured permanent employment and has left the program. This has greatly slowed the effort. The CDPHE has agreed to take up some of the slack to keep the program moving forward.

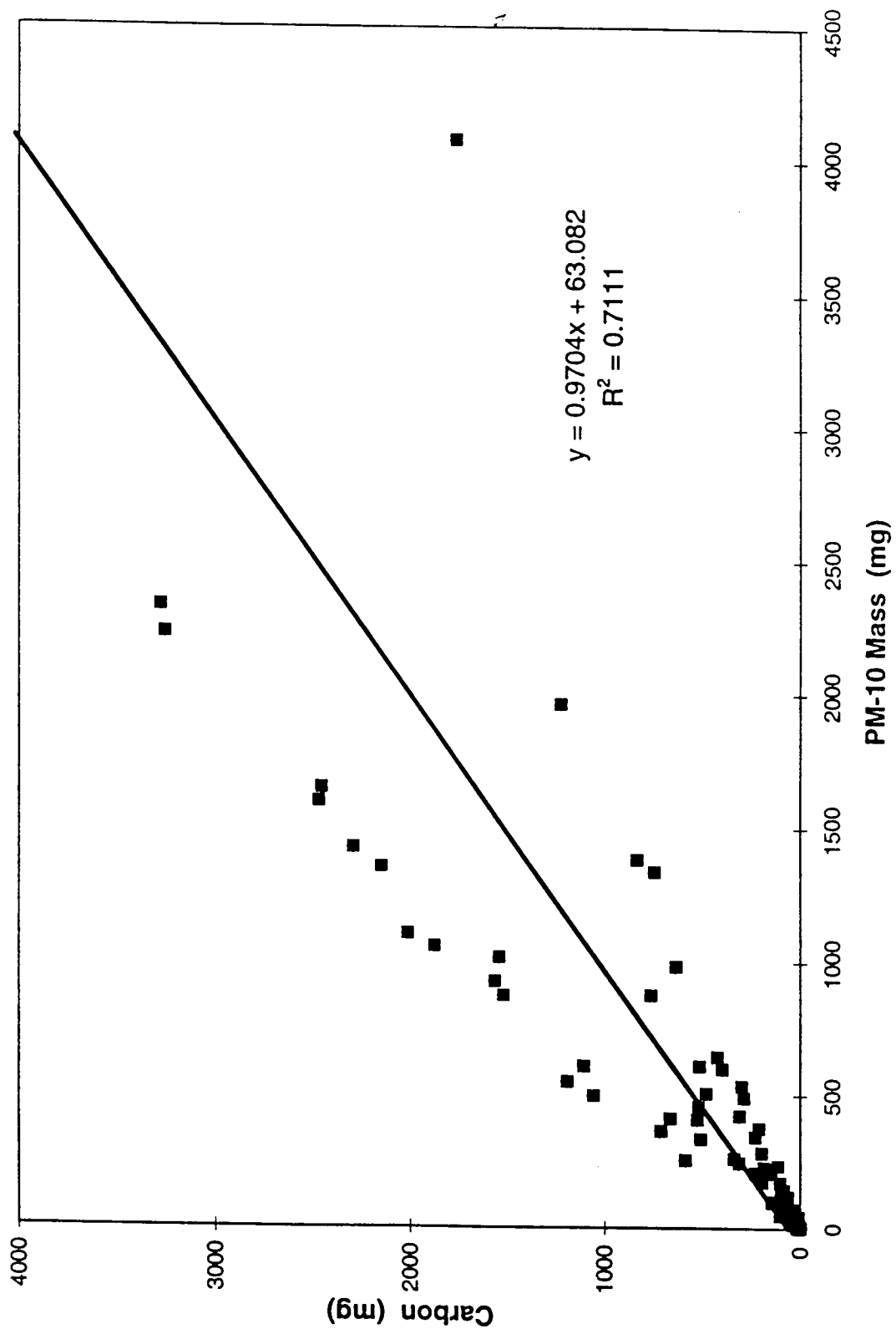
Plans

Analysis of the summer chemistry data will continue. Final validation steps for the summer data and the winter mass data will be taken. A draft report outline has been circulated for comment and it is hoped that parts of the report will be worked on in the near term.

Expenditures to Date

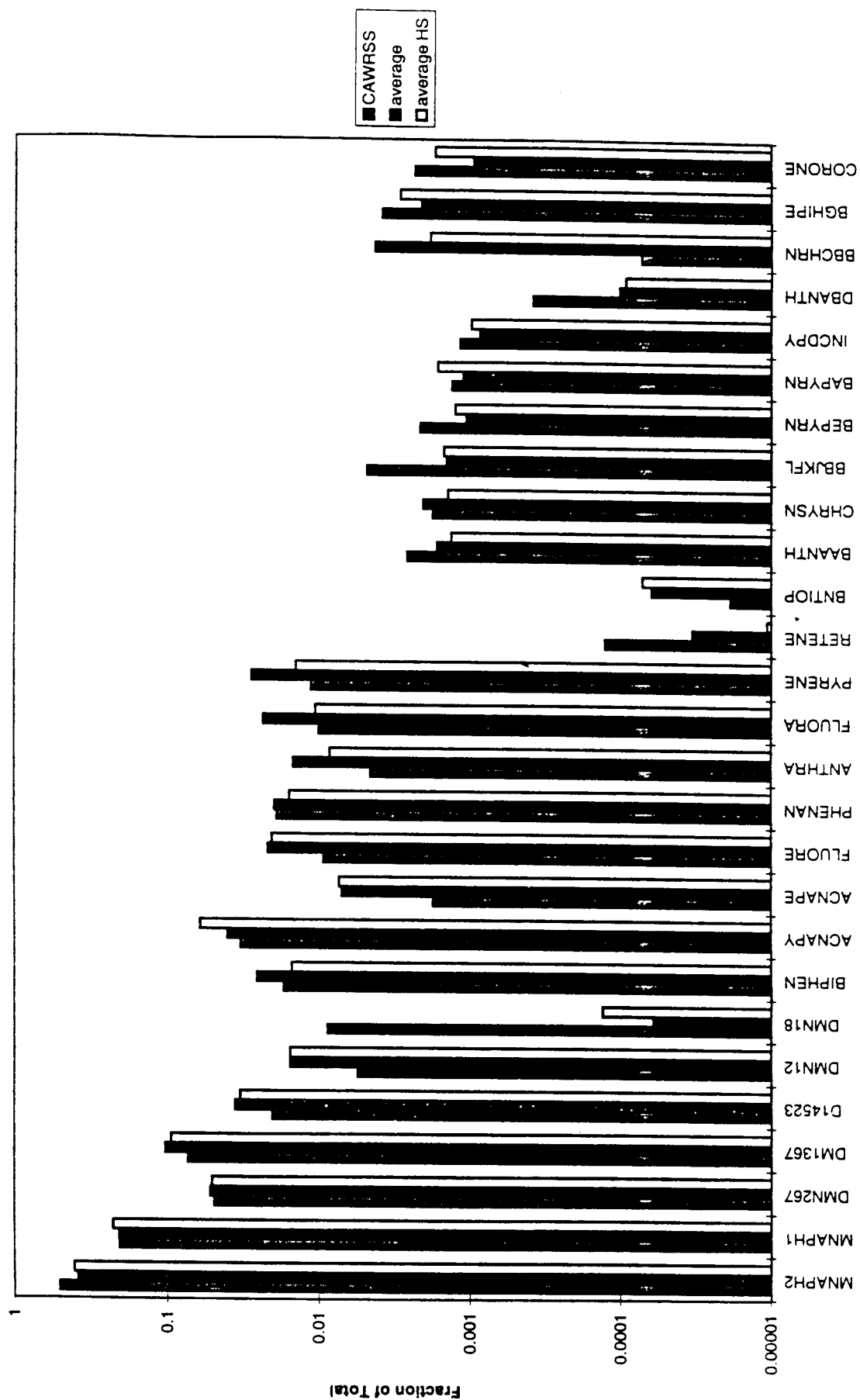
The program remains in budget.

PM-10 Mass vs. Total Carbon
(all Phases of FTP)

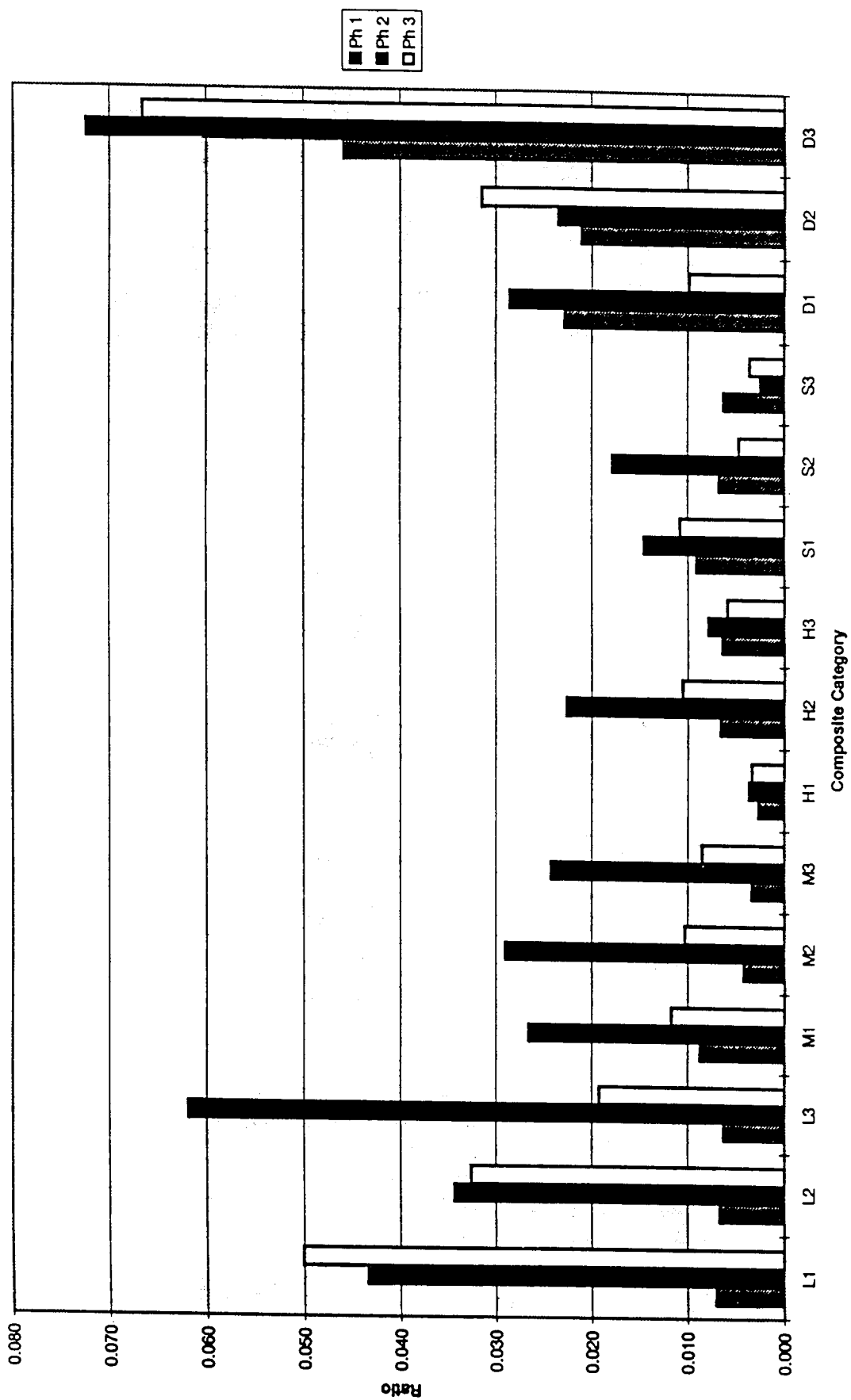


Run	MY	S/D??	Ph1 %OC	Ph1 %EC	Ph2 %OC	Ph2 %EC	Ph3 %OC	Ph3 %EC	FTP PM
DIESELS									mg/mi
4593	1993	D1	29.67	70.33	45.18	54.80	20.65	79.37	282.4
4605	1995	D1	33.78	66.24	66.79	33.25	55.03	44.99	143.3
4595	1994	D2	41.04	58.96	55.96	44.04	43.62	56.38	288.7
4589	1989	D3	67.60	32.40	66.79	33.21	57.80	42.20	3988.2
		Mean	43.02	56.98	58.68	41.33	44.28	55.74	1175.63
		Std dev	14.77	14.76	8.96	8.94	14.64	14.64	1624.87
71-80		n	4						
4510	1975	H3	88.10	11.88	96.30	3.69	83.08	16.96	110.9
4506	1976	H1	90.83	9.17	96.84	3.23	81.30	18.70	47.9
4551	1976		90.86	9.14	72.82	27.18	74.84	25.26	254.6
96078	1976		76.75	23.25	92.54	7.46	81.57	18.51	21.2
4538	1978		86.29	13.71	90.54	9.46	86.84	13.21	56.1
96105	1978		74.61	25.39	81.33	18.67	92.53	7.48	122.4
		Mean	82.13	17.87	84.31	15.69	83.95	16.11	113.56
		Std dev	6.69	6.69	7.86	7.86	6.53	6.56	89.16
81-85		n	6						
96047	1981	M3	63.49	36.51	60.32	39.68	48.46	51.54	21.8
96081	1981		47.40	52.60	91.87	8.47	78.79	20.94	3.2
96074	1983	H1	48.88	51.12	43.90	56.10	45.89	54.24	42.9
96186	1983	H2	94.41	5.59	94.86	5.20	93.44	6.56	68.9
96090	1983	M3	48.71	51.29	77.16	23.09	49.27	50.73	32.6
4479	1984	M1	92.10	7.94	90.94	9.17	81.63	18.49	28.3
4560	1985	H3	89.65	10.36	79.74	20.26	81.24	18.76	99.8
		Mean	81.22	18.80	85.67	14.43	76.39	23.64	57.39
		Std dev	18.85	18.84	7.41	7.45	16.41	16.40	29.11
86-90		n	7						
4482	1986	M1	38.79	61.27	89.68	10.32	48.16	51.84	16.4
4490	1986	M2	95.41	4.59	85.58	14.42	85.58	14.17	13.2
96010	1986		27.84	72.16	71.47	25.84	0.00	109.86	1.3
96164	1986		87.16	12.84	95.19	4.81	85.88	14.12	766.3
96071	1987	L2	58.82	41.03	91.42	8.48	75.01	24.73	6.4
96065	1987	M2	41.49	58.51	59.07	40.93	42.70	57.30	27.8
96068	1988	L1	57.83	41.90	93.88	6.12	48.17	51.83	2.1
96183	1989	H2	76.24	23.76	76.88	23.19	70.33	29.67	52.5
96180	1989		93.53	6.47	95.29	4.71	92.29	7.71	38.9
96044	1990	L3	65.98	34.02	94.32	5.46	66.66	33.34	9.7
96102	1990	L3	73.30	26.75	90.20	9.80	57.13	42.70	9.2
		Mean	77.26	22.75	89.17	10.79	71.60	28.36	27.58
		Std dev	10.11	10.11	7.35	7.42	12.88	12.83	18.75
91+		n	11						
96143	1991	L1	69.78	30.41	87.54	12.28	87.69	12.13	1.8
4554	1992	L2	43.89	56.11	58.30	41.70	63.21	37.22	7.3
4487	1992		49.30	50.70	82.80	17.20	51.34	45.40	0.9
4524	1994	L1	69.37	30.80	69.54	30.46	90.02	11.23	2.2
		Mean	58.09	42.01	74.54	25.41	73.07	26.50	3.04
		Std dev	11.65	11.56	11.47	11.52	16.36	15.10	2.51
SMOKERS		n	4						
96062	1986	S1	97.62	2.38	99.18	0.82	97.27	2.74	442.5
96201	1988	S1	96.85	3.15	99.53	0.47	97.29	2.71	551.5
96189	1983	S2	92.07	7.93	60.98	39.01	89.03	10.97	180.6
96192	1984	S2	77.07	22.93	86.09	13.90	37.73	62.27	144.3
4502	1971	S3	93.29	6.71	92.71	7.31	95.15	4.85	94.0
96161	1966	S3	83.53	16.48	89.11	10.85	79.44	20.58	277.4
		Mean	86.49	13.51	82.22	17.77	75.34	24.67	174.10
		Std dev	6.61	6.61	12.49	12.49	22.42	22.42	67.09
		n	6						

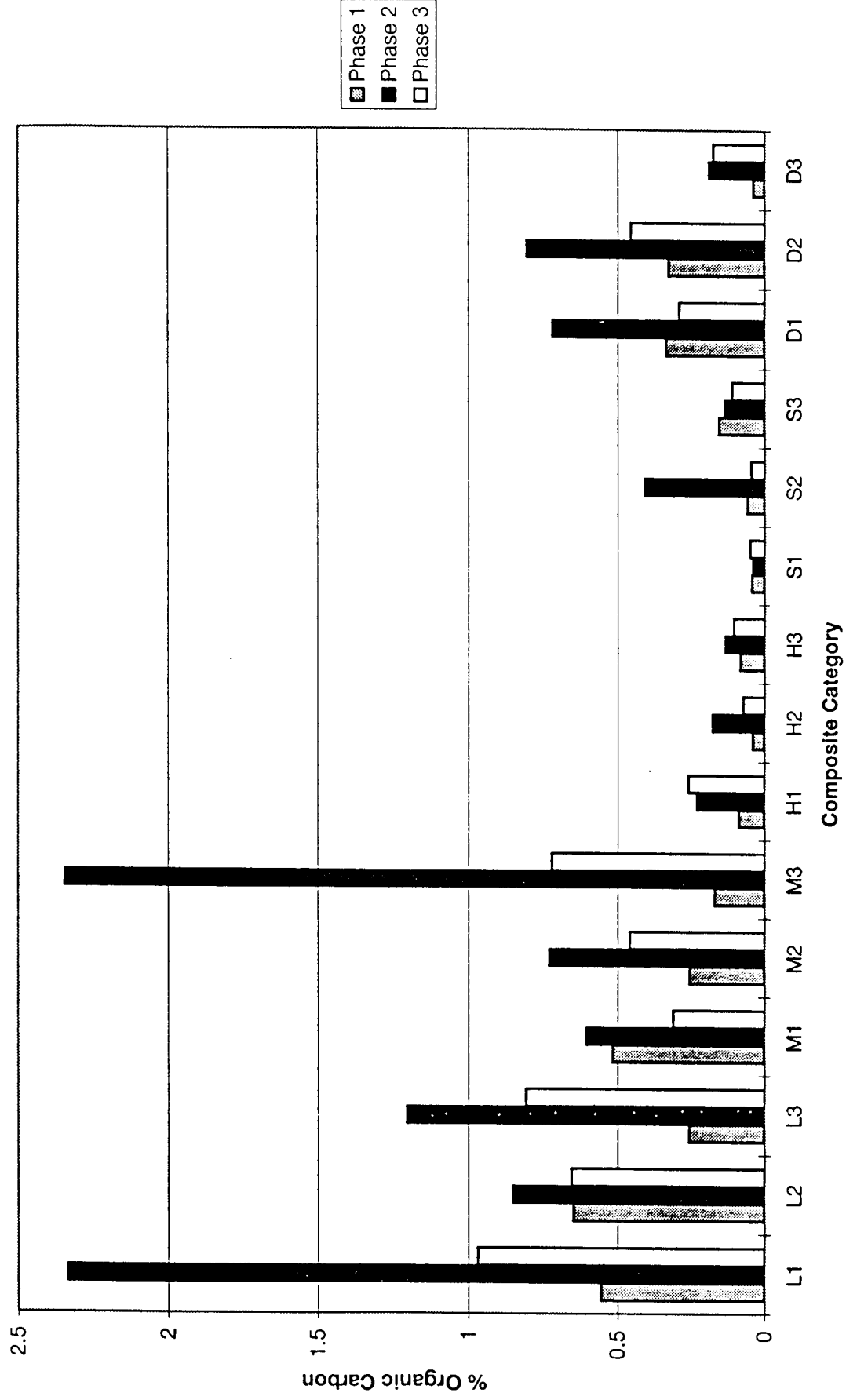
Comparison of PAH Profiles



Ratio of Total Dimethyl Phenanthrenes mg / Total PAH mg
(naphthalene excluded)



Dimethylyphenanthrenes as % Organic Carbon



Results from Back-to-Back IM240 Emission Tests
During the Winter

ID	Run	PM (mg/ml)	HC (g/ml)	CO (g/ml)	NOx (g/ml)	CO2 (g/ml)
310	4684	6.73	0.32	9.38	0.64	260.1
310	4685	3.83	0.23	5.42	0.58	271.6
317	4715	2.71	0.36	3.70	16.55	293.7
317	4716	2.69	0.29	5.34	1.38	293.0
332	4749	84.1	2.15	24.27	4.17	237.1
332	4750	97.6	2.17	26.93	4.03	240.5
349	4779	0.00	0.20	1.71	1.00	311.2
349	4780	0.00	0.08	0.90	0.77	313.3
337	4810	425	6.31	120.74	1.94	418.7
337	4811	468	6.97	126.31	1.88	415.5
362	4841	21.2	2.88	48.67	2.28	361.6
362	4842	14.7	2.96	39.70	2.53	362.0
377	4864	2.45				
377	4865	3.14	0.05	0.44	0.68	361.1
388	4904	679	0.30	2.05	2.62	445.3
388	4905	667	0.29	2.03	2.60	440.3
309	97032	2.24	0.11	0.96	1.44	355.7
309	97033	6.41	0.17	1.19	1.59	351.7
320	97069	23.9	5.46	26.58	2.70	441.1
320	97070	21.7	5.36	30.14	2.67	429.6
335	97100	36.7	1.99	23.77	2.75	439.5
335	97101	34.4	1.30	13.88	2.54	424.9
340	97131	1.77	0.00	0.84	0.42	242.0
340	97132	6.22	0.13	1.92	0.48	253.4
362	97162	9.02	1.95	42.96	1.40	294.8
362	97163	13.5	2.05	45.74	1.42	303.2
376	97196	0.97	0.01	0.70	0.17	226.7
376	97197	1.57	0.00	1.18	0.12	229.4
371	97227	7.71	0.69	7.22	1.19	237.5
371	97228	9.15	0.80	6.79	1.26	232.0
391	97258	320	0.42	0.90	0.48	236.2
391	97259	441	1.26	1.55	0.52	251.7

FTP Emission Rates From Replicate Tests

Vehicle ¹	Site	Period	Test Temp, °F	PM, mg/mi	HC, g/mi	CO, g/mi	NOx, g/mi	CO2, g/mi
1	CDPHE	summer	-	18	0.62	4.67	1.12	309
1	CDPHE	summer	-	5	0.52	3.32	1.21	306
2	CDPHE	summer	-	15	1.98	60.3	1.47	451
2	CDPHE	summer	-	14	1.95	61.7	1.42	461
3	CDPHE	summer	-	5.9	1.84	20.6	1.10	385
3	CDPHE	summer	-	6.0	1.72	21.2	1.02	380
4	EPA	summer	-	43	4.00	21.9	1.79	279
4	EPA	summer	-	33	4.33	23.8	1.91	300
5	EPA	summer	-	31	4.20	48.3	2.59	376
5	EPA	summer	-	62	4.63	25.2	3.33	396
6	EPA	summer	-	142	6.56	86.7	2.98	467
6	EPA	summer	-	147	6.33	86.6	2.72	460
7	CDPHE	winter	60	2.0	0.32	6.22	0.90	532
7	CDPHE	winter	60	4.5	0.28	6.00	0.96	543
8	CDPHE	winter	60	1.6	0.52	13.0	0.56	413
8	CDPHE	winter	60	2.2	0.40	9.01	0.63	418
9	CDPHE	winter	60	174	1.29	15.3	1.09	395
9	CDPHE	winter	60	161	1.55	16.3	1.15	396
10	CDPHE	winter	60	101	0.43	1.43	0.84	334
10	CDPHE	winter	60	56.7	0.49	1.33	0.84	335
11	EPA	winter	37	6.0	0.34	7.78	1.30	443
11	EPA	winter	32	16.6	0.32	7.21	1.18	431
12	EPA	winter	55	44.0	2.42	22.3	2.42	466
12	EPA	winter	55	37.2	2.27	25.2	2.35	427
13	EPA	winter	36	20.2	1.42	15.7	1.46	311
13	EPA	winter	34	22.3	1.69	15.6	1.38	273
14	EPA	winter	30	371	0.54	1.25	0.81	257
14	EPA	winter	31	293	0.54	1.35	0.82	259

1) Runs for the same vehicle listed in order of test date, starting with the first test